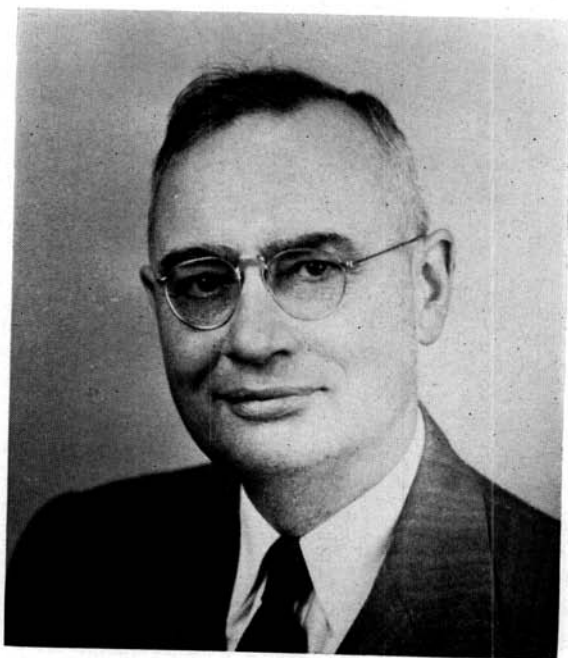


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THE TYRO CHEMIST'S UNANSWERED QUESTION

G. W. THIESSEN
Monmouth College, Monmouth



G. W. THIESSEN, *President*, 1954-1955

Beginning chemistry has its comic moments. I recall a former freshman chemistry student who offered, as an antonym to "volumetric" analysis, not "gravimetric", but "gravelmetric". Another labeled a portion of the "lead chamber" sulfuric acid factory the "blubber" tower, with no honor to Glover who designed it. A boy defined a "polar molecule" as "a molecule which would attract a compass needle", instead of "a molecule having sepa-

rated electric charges". With subtle logic, a girl offered "ice water" instead of "glass" as an example of a supercooled liquid. A meticulous Chemistry One laboratory mechanic, I am told, went through a long line to ask the storeroom man to supply the "inverted test tube" demanded by the laboratory manual for the impending experiment.

Occurrences like these indicate that beginning chemistry students do not think. This generalization is,

however, too sweeping to be valid. My object now is to defend the thesis that the thoughts of youth may be "long, long thoughts" even in the first chemistry course.

The situation which I wish to discuss usually develops within the first two weeks of chemical study. It may manifest itself in this way: The student has written $2\text{HgO} \rightarrow 2\text{Hg} + \text{O}_2$ and labeled the expression a "chemical equation". He has, moreover, performed the corresponding experiment, heated red mercuric oxide in a test tube, observed silvery mercury droplets on the tube walls, and watched a glowing wood splint rekindle in the evolved gas. He is then led to try igniting the smoldering wood with oxygen from hot barium peroxide. He succeeds, is delighted by his mastery of chemical mysteries, and probably misinterprets the experiment by writing $\text{BaO}_2 \rightarrow \text{Ba} + \text{O}_2$. After he corrects this, with the instructor's counsel, to the acceptable $2\text{BaO}_2 \rightarrow 2\text{BaO} + \text{O}_2$, he is ready for a more advanced problem. He gets it in SiO_2 , of which common sand is mainly composed. This substance contains a much larger percentage of oxygen than does either mercuric oxide or barium peroxide. The unwary student may be induced to write either $\text{SiO}_2 \rightarrow \text{Si} + \text{O}_2$, or $2\text{SiO} \rightarrow 2\text{SiO} + \text{O}_2$, and to test the proposition he has written with tube and burner and glowing splint. He of course observes no stimulated combustion to show oxygen is being released. He therefore immediately raises the question with which we now concern ourselves. He might frame it thus:

"Look—this reaction, for which I have set up a reasonable-looking bal-

anced equation, won't go. How am I supposed to know when something will happen, and when it will not?"

This is really quite a question. One has only to examine some beginning-chemistry texts, high-school or collegiate, to appreciate it. The attention of the student is diverted, generally, to other matters less difficult and less embarrassing to authors and instructors—for instance, to new reactions from which predicted products will be obtained. The general implication exists that some reactions that can be written in the form of balanced equations will go, and some will not go. The reason for this is perhaps non-existent, or too difficult for undergraduates to understand, or it may be none of the business of beginning students anyway.

Although the author of the textbook is remote enough from the discussion to be reasonably relieved of pressure, the teacher is not. And the question has a way of persisting. Let us, therefore, on behalf of the teacher and student, examine the tyro chemist's dilemma.

Part of this dilemma comes from labeling the written summary of a chemical reaction an "equation". In arithmetic and algebra, an equation is a statement of conservation through a process of rearrangement. In chemistry, it is this also; the equation states that mass is conserved in an ordinary chemical reaction. In mathematics, however, the *possibility* of the rearrangement is always taken for granted, whereas in chemistry the possibility always remains to be proved.

Another factor comes from physics, which our bewildered neophyte

may have also studied. That subject is beset with equations, and they have predictive power. Thus, for two forces of known magnitude and direction, a third force can be calculated to provide static equilibrium. The correctness of the calculation can be demonstrated dramatically by the composition-of-forces table. On this basis, the student expects any equation to do a respectable job of predicting. The chemical equation, which does not predict, he is apt to regard as a kind of conundrum. To satisfy him, we should be able to endow or supplement the chemical equation with predictive power, or at least to explain clearly why we cannot so endow or supplement it.

Mathematics and physics, which have contributed to the tyro's confusion on the point at issue, will now be invoked to help resolve it. Physics derives its potent mathematical equations by "static" and "dynamic" processes. In the former, forces or torques are set equal; in the latter, energies are set equal. In either case, useful, predictive formulae result. (Parenthetically, note that in physics or mathematics, a formula *is* an equation; whereas in chemistry a formula is only a *part* of an equation, as a word is part of a sentence.)

The static process might seem to bear some promise. The movement of electrons or atoms to and from molecules or parts thereof will constitute the reaction under consideration. If the magnitudes and directions of all forces on all parts of this atomic system were known, the directions and extents of all movements within it might conceivably be cal-

culated. Then a decision could be made as to whether the resulting total displacement would be, or would include, the reaction under consideration.

A practical difficulty intervenes. It is impossible to set up general equations for even three gravitating bodies, which will fully and uniquely predict the motions resulting from mutual interaction. If now the three bodies are replaced by myriads of millions, possibly of several diverse kinds, each heterogeneous, and each with electrostatic and magnetic fields in addition to its gravitational field, the possibilities for complexity are fantastic. Previous motions of molecular and submolecular units and the special restrictions of the quantum theory contribute prohibitive problems. The static method of physics, as a means of predicting the possibility of a reaction, is beyond consideration.

The dynamic process is therefore considered. Indeed, the tyro will move automatically toward it as he pursues his first chemistry course. The introduction may well be two experiments shown to him in quick succession. In one, steam (hydrogen oxide) is passed over hot iron, producing iron oxide and hydrogen. The hydrogen is duly collected and burned. The chemical equation $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$ is written by the demonstrator, and believed by the student because of the concrete evidence before him. In the other experiment, hydrogen is generated, dried, and passed over hot iron oxide. A visible evolution of water occurs, and iron metal is formed, sometimes in a fascinating pyrophoric modification. Again, an

equation may be written, and accepted. It reads: $4\text{H}_2 + \text{Fe}_3\text{O}_4 \rightarrow 4\text{H}_2\text{O} + 3\text{Fe}$. The second equation is obviously the reverse of the first. Both, in fact, can be written as one, with the use of two arrows, thus: $4\text{H}_2 + \text{Fe}_3\text{O}_4 \rightleftharpoons 4\text{H}_2\text{O} + 3\text{Fe}$. The student here encounters the reversible reaction. He is led to think of the results of sealing iron and water in one flask, and iron oxide and hydrogen in another, and heating both to reacting temperature. The concept of equilibrium in a chemical reaction is now a part of his equipment.

Reaction speed, he learns, is moles per liter per minute of substance converted. With fixed temperature and catalytic conditions, reaction speed is proportional to concentrations, in moles per liter, of things being consumed. A mathematical equation applying this "law of mass action" can be set up for each of the two facets of the reversible reaction. At equilibrium, the two speeds can be equated. The resulting equation can be solved for the ratio of the two velocity constants. This ratio can be replaced by a single new constant, called the "equilibrium constant". Representing concentrations by square brackets about the formulae of the respective substances, the equilibrium constant for the reversible reaction represented above appears as

$$K_e = \frac{[\text{Fe}_3\text{O}_4] [\text{H}_2]^4}{[\text{Fe}]^3 [\text{H}_2\text{O}]^4}$$

(The rudimentary constant given above needs many refinements before being useful for precise calculations. The refinements are not here presented because they are not pertinent

to the present discussion.) This equilibrium constant will remain constant, no matter how the relative concentrations may be varied, if only the temperature remains constant. Even catalysis cannot change it.

The inquiring tyro may transfer the new concept to the old problem, by assuming that all reactions possess reversibility, but in highly-variable degrees. Since silicon will combine with oxygen to form silicon dioxide, the reverse reaction should also occur. This reverse reaction is the decomposition of silicon dioxide into silicon and oxygen. The tyro probably melted his test tube trying vainly to produce enough oxygen from it to get a test; from which he must conclude that the equilibrium constant for this reaction,

$$K_e = \frac{[\text{Si}] [\text{O}_2]}{[\text{SiO}_2]},$$

is very small at the highest temperatures attainable in glass vessels. He has, of course, no answer to his demand for a predictive power over chemical reactions. He does have, however, the means of asking his question in a better form. He may ask now: "How can I calculate in advance the equilibrium constant of this reaction for which I have written an equation?" The new form is better than the old because it is cast in the inherently precise language of mathematics.

It is evident that if the equilibrium constant be given, the equilibrium yield of oxygen can be calculated, if also initial amounts of starting material, and byproduct, if any, and the volume of the reaction

chamber be known. It is also evident, however, that the necessary equilibrium constant is as yet available only by virtue of the reaction having been done at least once, with measurement of the equilibrium concentration. Our tyro has become able to calculate equilibrium yields for a variety of "scrambles" of starting materials and products initially mixed. He cannot, however, grasp the predictive power he seeks because he cannot write the equilibrium constant before the reaction has ever been done.

The equilibrium constant changes with changing temperature. This fact does not make necessary a separate experimental evaluation of K_e for each new temperature. If the heat evolved during a reaction is known, an equilibrium constant at a second temperature may be calculated from an equilibrium constant given at a first temperature. Also, the heat of reaction is an additive quantity which for a given reaction can sometimes be calculated from other reactions already tabulated in the literature. It is still necessary to carry out the reaction once to get its equilibrium constant at some temperature, of course, and fundamental predictive power still eludes our tyro.

Heat has been injected into our dynamics; this makes it "thermodynamics". Thermodynamics is "infested" with calculus. Calculus was involved in the equation for shifting the equilibrium constant with shifting temperatures, and the end is not yet. Calculus will be viewed by the student with suspicion and aversion. To him it will be a barrier rather than a ladder between

him and his goal of predictive power. And that goal is not yet even in sight.

The goal is, nevertheless, just around the corner. Consider the reacting substances in question to be in equilibrium inside a box. Imagine pumps available to move ingredients into the box, and to move products from it. Let each pump have between it and the box a diaphragm, permeable to only its own component of the reacting system. Let all this apparatus be at a constant temperature. Then imagine the pumps all operating very slowly, so as to transfer a mole of product from the box, and also the necessary moles of byproducts from it, and of ingredients into it. Let the amounts of materials of all sorts in the box be the same after as before. Calculate the net work expended in operating the pumps. From this net work, the temperature, the pressures of all the ingredients in their separate pumps, and from the universal gas constant, you may derive the logarithm of the equilibrium constant. The net work mentioned above is the "free energy change" of the reaction. The equation connecting the free energy and the equilibrium constant is especially simple if reactants and products are all at "standard states" before being put into the equilibrium box or after being removed from it. Standard states are attained for gases by having them at one atmosphere pressure. Solutes are in standard state when at molar concentrations. Pure solids and liquids have their own special standard states.

Free energies have been assigned for many chemical reactions. Most

reactions thus treated are formations of compounds from their elements, all ingredients being in appropriate standard states. Free energy changes thus recorded are usually for 25° C. If a new reaction whose extent is to be predicted can be shown equal to any series of reactions for which the free-energy changes are known, its own free-energy change can be calculated by simple summation. When its own free energy change can be calculated, for usual standard-state conditions, its equilibrium constant can be estimated for 25° C. From the one equilibrium constant, that at any other temperature can be estimated, if the heat of reaction be known. If the heat of reaction be known at one temperature, and if the equations for the specific heats of all the reaction ingredients be known also through a sufficient range, the heat of reaction and the equilibrium constant can be calculated at the new temperature. Since both the standard free-energy change and the heat of reaction at some one temperature may conceivably be calculated from data derived from reactions other than the one being studied, it becomes possible, to calculate the equilibrium constant in advance of doing the experiment. The tyro's question has been answered!

Obviously, the answer isn't of any practical use to the beginning student of chemistry. He lacks the mathematical and physical training needed to apply it. He couldn't be sure of finding the needed data for an arbitrarily-selected case. If he did have all the knowledge and all the data, he would need to figure industriously for half a day before he

would have his prediction ready. In most cases experiment would be quicker than calculation.

We have also ignored another important item, which is the rate of approach to equilibrium. To make perceptible progress toward equilibrium might require a century or more. If the student has calculated, for a hypothetical reaction, an equilibrium constant which promises him a useful yield, he can not thereby prove that this yield would become available to him before he died of old age. If he would solve this new problem, he must confront a whole new area of pseudo-thermodynamics. The new area possesses more complex equations and fewer available data than does the old.

In short, the thermodynamic solution of the problem is in reach, but barely. It is so laborious and cumbersome that it might as well, almost, be as unattainable as the static solution first contemplated.

Modern theorists have turned to the probability of the presence of electrons in assigned locations as a basis for predicting the extent of an hypothesized reaction. This third plan, applied loosely and qualitatively, can readily lead to conflicting predictions. A book advertisement received recently stated that "electronic theory is presented as an aid to understanding and memory rather than as . . . a predictive tool"; I sympathize with this viewpoint. Used quantitatively, the third plan leads to mathematical calculations even more involved than those of classical thermodynamics. So difficult are these calculations that they have scarcely been attempted for the interaction of any system more

complicated than that consisting of one proton and one electron.

We left our inquiring beginner with his smoldering test-tube of sand outside the mathematical barriers over which we have passed. He is smoldering internally also when we return to him, for he feels that he is the victim of a mean pedagogical trick. He handed us an unanswerable question. We return it to him, and it is still, for him, unanswerable. Is there anything we can tell him about predicting whether a reaction will proceed to a useful extent within a reasonable time?

About all we can say to help him is this: "The balanced chemical equation has no inherent qualitative predictive power. After you write the reactants on the left, you have no assurance of any measurable amount of product appearing to represent the right-hand side. If conflicting choices confront you, the equation does not help you choose. The right-hand side of the equation, for any practical purpose, must be written on the basis of knowledge, or guess. The knowledge may be your own, gained by direct test. Such must be recorded or memorized to remain available to you, and pub-

lished if it is to be made available to others. The knowledge may be that of others, which you have drawn from their records.

"The guess is an entirely legitimate procedure. It need not be an entirely blind guess. Atomic diagrams, periodic-chart relationships, and homology in organic compounds can all suggest analogies between familiar, memorized reactions and unfamiliar ones whose outcomes are to be predicted. The more examples you know, the more easily and exactly you can predict. Therefore, in the beginning of your chemical study, you must become familiar by rote with as many examples as you can. You must also learn to consult quickly the records for more information than you can carry unassisted. Whether we like to have it so or not, chemistry is still far from being a predictive science. It is still largely an experimental art."

And finally, the rest of us may draw the modest moral that there is hope for the future of science, so long as there are some people in its ranks who ask unanswerable questions, and others who try to answer them.