

In The Classroom

Chemical Kinetics: As Important As The Second Law Of Thermodynamics?

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The second law may be “time’s arrow” but activation energies (chemical kinetics) prevent second law predictions from occurring for femtoseconds to eons. This is humanly important: Activation energies not only protect all the organic chemicals in our bodies and our oxidizable possessions from instant combustion in air, but also our breakable skis and surfboards (and legs) from disastrous fracture. Murphy’s Law is often applied to chemical and physical mishaps—things going wrong. But things do *not* always follow the second law and burst into flame or break! Chemical kinetics is the reason Murphy’s Law usually fails.

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Introduction

The second law of thermodynamics is awe-full in its breadth and depth of applicability—from quarks to cosmos from chemical reactions to perpetual motion machines. Its supremacy has never been expressed more eloquently than by Sir Arthur Eddington [1] many years ago, with the firm conclusion: "...if your theory is found to be against the Second Law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation." Sir Arthur had previously summarized the second law's pertinence to our intuitive sense of time by describing it as "time's arrow"; however, when the vital role of kinetics in chemical reactions was recently coupled with his aphorism to yield [2]: "The second law of thermodynamics is time's arrow, but chemical kinetics is time's variable clock." unexpectedly, some chemists' reactions were lukewarm [3]. Certainly, everyone agrees that the field of kinetics is basic to understanding chemistry but, equally certain, it is not as far reaching nor as fundamental to understanding all of nature as the second law. How can the two be coupled and thus implied to be of comparable importance? That question is answered in this brief article.

The Teaching of Chemical Kinetics: *Rates of Reaction, Energies of Activation*

Of necessity, a good professor makes sure that a student's first introduction to reaction rates is via thoroughly studied, mathematically simple reactions. This usually means that the mechanisms are also simple, but it surely does not imply that the substances discussed are common everyday materials. The decomposition of NOBr or the reaction of F₂ with NO₂ do not involve chemicals that students encounter in large quantities in their dorm rooms or on the quad. As the subject of kinetics is further developed in texts or lectures, additional substances, which are also far from a student's daily experience are used. This is part of learning, as is hearing that most thermodynamically spontaneous reactions are hindered or blocked by the bond-breaking requirements that lie behind energies of activation. Activation energy (E_{act}) is thereby seen as the energetic barrier that prevents the second law from being obeyed instantly. Students, however, may tend to recall the kinetics-thermo conflict most vividly in connection with exotic chemicals. NOBr may stick in their minds even after they are shown that, in our oxygen-rich environment, the same kinetic hindrance applies to any combustible substance.

The Second Law is Meaningless Without Chemical Kinetics?

Professors rarely mention oxidations of organic materials in their initial development of rates of reaction because the kinetics and mechanisms are so complex. Still, even a first-year student who can merely balance the atoms on both sides of an equation does not find it complicated to calculate ΔG for the reaction of oxygen with organic compounds to yield CO_2 and water. The conclusion is breathtaking to a novice: All the free energies of oxidation of organics with oxygen are negative; therefore, no organic substance, including every one essential for life—no organic substance could exist in the presence of air if it were not for the activation energy barriers that impede the rapid execution of the second law. Without chemical kinetics (fundamentally, without the dominance of bond breaking over bond forming in reactions) there would be no life in the universe. Air makes life impossible unless the barrier of E_{act} is present.

The second law is supreme, but how meaningful would it be without the intelligence of any life form to discern it? Life cannot exist without multitudes of obstructions to chemical reactions deemed spontaneous by the second law, the E_{act} obstacles. What better justification is there for insisting that to properly describe the behavior of matter in the real world in which we and other life forms are present, Eddington's description of second-law action must be constricted by: "but chemical kinetics is time's variable clock"?

Chemical Kinetics are the Reason Murphy's Law Usually Fails

Murphy's Law originally was applied to human foibles and our working with complex systems [4]. Obviously it is hyperbole, but it can be a humorous relief for our frustrations. Frequently, however, the "Law" is extended to situations or events that annoy or harm us, yet principally involve the behavior of chemical substances and material objects, not other people. We may react with, "Why do things go wrong?" or even "Why me?" In these situations, then, it is time for chemists to explain the bases of such happenings both to nonscientists and to scientists in other fields:

- Things usually don't go wrong.
- Common substances do not instantly change in air or moisture.
- Most objects hold together and do not immediately break.
- The reason for stability is chemical kinetics, implemented by activation energies.

- When physical misfortune does occur it is usually due to energy input that exceeds the critical E_{act} of some component.

Would it not be useful for all professors in beginning chemistry to pose questions that involve several dramatic examples of E_{act} obstructing thermodynamically spontaneous reactions? “Why can wooden chairs or toast or library books be exposed to air and not vanish instantly? Why do all of us humans not spontaneously combust?” Just asking students to look around their lecture room would allow the lecturer to underscore the enormous importance of activation energies in oxidation: Only the cement and plaster of the room would be there at that moment if there were no E_{act} . If, in that room and just outside it, activation energy were suddenly “abolished,” all students (and instructors), everything not already in its most stable oxidation state—clothing and other fabrics, paints, polymers, steel, aluminum, and lecture bench—all would vanish in a fireball to become carbon monoxide, carbon dioxide, nitrogen oxides, and hot metal oxide particles as sufficient oxygen flowed into the room. Their bikes outside would be changed to incandescent showers of metal oxide while their cars would explode while expelling huge quantities of glowing metal oxide dust, plus the gaseous CO, CO₂, and nitrogen oxides from paints, plastics, rubber, upholstery and oils. Those sentences alone would be enough (without describing a worldwide scene of a wasted planet after the destruction of all cellulosic and oxidizable materials, limited only by the available oxygen) to fix in students’ minds the importance of chemical kinetics to existence and to our prized artifacts—with E_{act} as the guardian of kinetic control. It is only when an ignition source is provided (as in the oxidation of combustibles) or a catalytic, E_{act} -decreasing, agent inserted (as in the oxidation, corrosion, of metals) that Murphy’s Law wins. “Why do things go wrong?” has a ready answer in chemical events that incidentally or disastrously upset humans, that is, “when activation energies are exceeded.” Oxidative destruction of our prized artifacts, like our homes, bikes, or cars is prevented by E_{act} ; thus, quantitatively and statistically, things most often do not go wrong chemically. Poor Murphy is mainly a loser thanks to chemistry’s kinetics.

Breaking Things: “Physical Change” That Causes Human Distress

Probably the majority of unpleasant material happenings in our lives do not involve chemical changes. Murphy’s Law more often seems to threaten us daily by the breakage or wearing out of some thing that we need or treasure. Wear in machines (or tires) is due to multiple fractures of clumps of atoms or molecules from a solid object.

In tearing a car fender in an accident or breaking an arm—or even the terrifying disaster of having our house destroyed in a tropical hurricane or a California earthquake—the things altered in these distressful events haven't been chemically changed. Fracturing solids is a physical change, not related to chemical change, is it not? Certainly, the free energy of the bulk of the material in a ski before and after it is broken is essentially the same, but interatomic or intermolecular bonds have been split and new ones formed along and near the break line in the process. So, activation energies are involved. Unfortunately, no E_{act} that is general to a chemical type of solid, even if it is a relatively pure cellulosic or phenolic substance or steel, can be determined as for a chemical reaction mixture. This is true because of the variable non-fundamental factors in the fracture of a particular solid object: its shape, history of fabrication, strains and defects within it, minor and trace elements and their sites, as well as many other considerations including the rate of application of load at a specific point on the object. However, as has been described and is intuitively obvious, a plot of the mechanical force or load that can be applied to some thing at a particular point until it breaks is at a maximum for the specific situation and object immediately prior to its fracture [5]. This maximum can be defined as the $E_{act, solid}$ for that individual event because it is the energy input required to initiate the process of fracture; it bears the same relation to breaking a solid that a chemical E_{act} has to permitting a spontaneous reaction to occur. They are each the minimal input of energy required before change occurs, either physical or chemical. If the physical change or chemical change to which they apply is undesirable to us, it is the $E_{act, solid}$ or E_{act} that protects us from mishap or even tragedy. “A fractured leg in a ski accident, a corroded fitting in Chuck Yeager's X1 rocket plane that nearly killed him, a broken timing gear in a Corvette, a fire in a fraternity house started by a forgotten cigarette, a California freeway collapse in an earthquake—all these are examples of activation energies being exceeded, whether in chemical reactions or physical fractures. They involve “things going wrong” in people's lives. ...Activation energies in chemical and physical events protect us and our prized objects from undesirable as well as disastrous change [5].”

Conclusion

Purely from a human viewpoint chemical kinetics is as important as The Second Law of Thermodynamics. Neither humans nor any other organism could exist in air if E_{act} was not an energetic barrier to the second law because all organic compounds are

thermodynamically unstable in oxygen. The infinite variety of solid objects that we use or prize are held together, despite their thermodynamic metastability toward violent external energy flows, by chemical bonding, and thus they are protected from change by $E_{act\ solid}$. Equally vital to us all, the many essential or treasured combustible and oxidizable things about us, from forests to homes to steel artifacts, are protected from change in air by activation energies. Fortunately for us “The second law of thermodynamics is time’s arrow but chemical kinetics is time’s variable clock.”

REFERENCES

1. Eddington, A. S. *The Nature of the Physical World*; Macmillan: New York, 1928; p 74.
2. Lambert, F. L. *Chem. Intelligencer* **1996**, 2(2), 20.
3. Private letter from a professor in a northeastern U. S. university and conversations with California college faculty.
4. Bloch, A. *Murphy’s Law*; Price/Sloan/Stern: Los Angeles, 1977; pp 4–52².
5. Lambert, F. L. *J. Chem. Educ.* **1997**, 74, 947.

² There are enough erroneous ascriptions of Murphy’s Law to justify its existence solely from the mis-citers. Bloch, the least academic source, still has the most authoritative account from George E. Nichols, the Quality Assurance Manager of the NASA Viking Project in 1949. He first assigned the title “Murphy’s Law” to a statement from Captain Edward Murphy, Jr. about a technician who had wired a strain gage incorrectly, “If there is any way to do it wrong, he will.” The law was then rapidly generalized (applied to objects as well as to individuals) on the project and throughout the world. Even a recent informal scholarly book, *Why Things Bite Back* (Edward Tenner, Vintage: New York, 1997; pp 22–23), has a slightly misleading account and also misspells Bloch’s name.