Why Don't Things Go Wrong More Often? Activation Energies: Maxwell's Angels, Obstacles to Murphy's Law

Frank L. Lambert
Occidental College, Los Angeles, CA 90041*

Murphy's law is a fraud. He didn't check the data before writing it. But why does it fail? Why don't material things go wrong and therefore upset each of us every minute? Wooden roofs in Malibu don't constantly burst into flame. Forest fires don't erratically happen by themselves and threaten all of us living in groves of trees. The Golden Gate Bridge cables didn't change to iron rust and the bridge collapse before being painted the first time. Skis do not break as readily as Waterford crystal goblets and tires don't wear out after just ten miles even on the rockiest road in the world.

The Second Law Is Time's Arrow—But Chemical Kinetics Is Time's Clock

Most chemistry students know the reason for Murphy's failure in the oxidative examples above: it is activation energies.[1] Thermodynamically spontaneous processes such as combustibles catching fire or the complete oxidation of iron do not occur instantly in air despite the huge free energy differences between products and reactants. The second law of thermodynamics is indeed time's arrow, but chemical kinetics is its clock (*1*). Activation energies set the timing of events involving materials because they determine the rate of chemical reactions at a given temperature. They obstruct or delay the second law for microseconds to millennia.

Disasters can occur if chemical systems that are important to us are supplied with sufficient energy to surmount their particular activation energy barriers. Only a pedantic chemist would write the preceding sentence to summarize the news of a fire on an aircraft carrier's refueling deck—"One static spark set some jet fuel on fire, which spread to an armed plane, whose bomb load exploded owing to the intense heat, quickly forcing… ." When activation energy barriers are overcome by even a relatively modest energy input, thermodynamics governs. Spontaneous reactions then can take place rapidly and, if widespread as well as strongly exergonic, enormous heat evolution can occur to cause a human calamity.

Activation Energies as Maxwell's Angels

Thus, it is clear that oxidizable substances and human artifacts made from them are kept from immediate destruction in our oxygen-rich environment by activation energy barriers. Essentially, activation energies act as "Maxwell's Angels" for many kinds of our prized objects, in the sense of protecting patterned paper books and elegantly organized wooden houses and their contents from changing into random molecules of carbon dioxide and water. Maxwell's demon can merely select particular atoms or molecules to partition them into thermodynamically improbable groups. The many Maxwell's Angels of activation energies keep humanly selected thermodynamically improbable groups of atoms—our valued objects—from changing into random or otherwise humanly undesirable groups. They protect us from Murphy's law being valid. Only when they are defeated does Murphy look wise.

Nonchemical "Things That Go Wrong"

But the majority of material things going wrong in our lives do not involve chemical changes that have characteristic activation energies. Murphy's law more often seems to threaten us each day by the breakage or wearing out of our treasured articles and invaluable machines. Wear in gears or tires is due to multiple fractures, microscopic clumps of atoms or molecules being broken off a solid object. It may be troublesome or life threatening. Breaking a surfboard, smashing a car fender, fracturing a leg—or even the catastrophe of having our house torn apart in a California earthquake or a Florida hurricane—the things broken or made chaotic in these ways haven't been chemically changed. Fracturing solids is a nonchemical, extra-thermodynamic process—a physical change. Or is it?

The Chemical Aspects of Physical Change

Certainly, the free energy of the bulk of the material in a ski before and after it is broken is essentially the same. But the break occurs because interatomic or intermolecular bonds are split. It is the strength of these bonds throughout an object that obviously is one of the barriers that keep solid things in their particular patterns. Therefore it might seem logical that simply measuring bond strengths along a probable break-path in a solid would give some indication of how much energy is necessary to fracture it and destroy its pattern. Because this energy would involve bond rupture and be the minimum required to get over the barriers protecting the solid from breaking, it would be functionally equivalent to an activation energy in a chemical reaction.

The Complexity of Breaking a Solid

Even though the fracture of a solid depends on bond strengths along the break-line, the pathway and the energy required for the process are affected by many other factors: the way an object was made, its shape, its ratio of surface area to volume, the strains and defects present within it, whether it is a brittle or ductile material, and the rate of application of energy to it. Complex rearrangements of atoms (or molecules in a covalent solid) near and distant from the break are additional energy-requiring events. Thus, the barrier to breaking—the activation energy of fracturing a particular solid—does not refer to a unique concerted process of bond cleavage and new-bond formation as does an activation energy for a particular chemical reaction.

A Generalized Activation Energy for Solid Fracture

A qualitative plot of the effect of load (mechanical force) being applied to a solid object until it breaks is shown in Figure 1 (*1*). Line A depicts the external load affecting the object; B, the object's free energy during the process; and C, the object's "pattern desirability" to a person or a societal group.[2]

---

*Present address: 2834 Lewis Drive, La Verne, CA 91750.

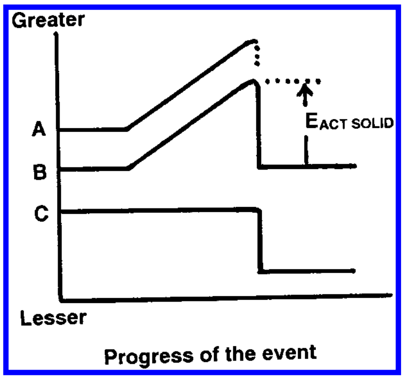

Figure 1. Load (“mechanical force”) being applied to a solid object until it fractures. A: Externally applied load. B: Free energy of solid. C: Human “pattern desirability” of object.

Figure 1 represents the course of an event wherein increasing load or force is applied at some rate to a particular volume element of a solid having a specific fabrication history and a human-desirable pattern. All lines, A, B, and C, are initially horizontal to indicate reference states before the application of any external force or load. At first the free energy of the solid (line B) increases regularly as greater and greater load (line A) bears upon it. Then, just prior to its break, complex changes may occur inside a brittle solid, as indicated by the slight rounding over of the free energy line in B.[3] If the external load acting on the solid is increased until fracture occurs, line B immediately falls to the starting free energy value (except for transient heat and the kinetic energy in any flying fragments). Line C drops radically after the break, a rough indication of the far lesser human value for the two broken pieces as compared to the original object.

Because the free energy of the solid (shown in B) is increasing due to the externally applied load (in A), the maximum of this free energy at the moment of break is that critical energy required to initiate breakage of the object, $E_{\mathrm{ACT\ SOLID}}$. Thus, $E_{\mathrm{ACT\ SOLID}}$ represents a function comparable in effect to the free energy barrier height measured by the activation energy for chemical processes.

Randomness in the Breaking of Artifacts

Figure 1 is the diagram for one break of a solid object. In a hurricane, energy is successively applied to many fragments of the first break so that houses become scattered parts; boards sometimes are splintered into bits. In the 1995 Kobe earthquake, even concrete structures were torn apart and many portions of them reduced to rubble. At each successive step, the qualitative plot of Figure 1 applies—additional load is supplied to break parts of the original and then those parts are again broken. When the activation energy barriers of a solid are repeatedly exceeded, it is pedantic to state merely that the pattern desirability to humans, indicated by line C, decreases markedly at each fracture and approaches total randomness as a limit. Torn-apart houses and squashed cars under a collapsed parking structure far more vividly illustrate the existential impact of repeated fractures than such academic phrases as “decreased pattern desirability” or “multiples of line C”.

Activation Energies as Protective Barriers Against Disaster

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. The counterview is even more important both for a rational philosophy and for a significant comment in many kinds of chemistry lectures: Activation energies in chemical and physical events protect us and our prized objects from undesirable as well as disastrous change.

Finnegan’s Law

Murphy’s law is a fraud so far as the behavior of physical objects is concerned. Surfboards don’t always break or gears instantly wear out or houses catch fire without a heat source. Statistically, Murphy hyperbolizes a very small probability. Reality is closer to what might be called Finnegan’s law: “Whenever material things hang together and go right, it is activation energies that keep them that way. Activation energies are what usually protect us from ‘things going wrong’.”

Acknowledgment

I thank Richard. E. Robertson of the College of Engineering of the University of Michigan for invaluable advice concerning the fracture of solids.

Notes

1. Fundamentally, of course, activation energies in chemical reactions are due to the dominance of chemical bond breaking over formation of new bonds in the transition state, the “critical structure of chemical reactions” (*2*).

2. The function identified with line C is related to the negative entropy of the fabricated object compared to the materials of its construction. It is difficult or impossible to quantify, especially in the case of treasured or unusually useful artifacts. (Economic value is probably the best extra-thermodynamic measure.) Because of this overlay of human preferences, the qualitative descriptor “pattern desirability” is preferable to any phrase involving entropy.

3. The free energy of a ductile solid (as indicated by its “line B”) would have a more rounded approach to a break, indicating that deformation and even permanent deformation can occur before fracture. In the case of either a brittle or a ductile solid, if the applied external load is removed before this curve, which indicates a decrease in the rate of change of the solid’s free energy, the solid can recover. To the extent that its free energy returns to its original value with incidental evolution of kinetic energy, it and line C, the human valuation of the pattern of the object, will be unaltered.

Literature Cited

1. Lambert, F. L. *Chem. Intelligencer* **1996,** *2*(2), 20–25.
2. Bauer, S. H.; Wilcox, C. F., Jr. *J. Chem. Educ.* **1995,** *72,* 13–14.