This empirical rule is known as Hammond's postulate.

Wales shows (*1*) that the transition point and one of the local minima often emerge from a single non-Morse critical point at a fold catastrophe. If the two points are sufficiently close that the cubic fold catastrophe function remains a reasonable approximation to the energy along the reaction path, the basis of Hammond's postulate becomes clear: The higher energy minimum and the transition point correspond to the relatively closely spaced minimum and maximum of the cubic catastrophe function and share a common parent structure at the non-Morse critical point. The lower energy minimum lies at a considerable distance down the descending left-hand tail of the catastrophe function and is not related by shared parentage to the transition point.

Wales also shows that for fold catastrophes, a quantitative relation holds between the seemingly independent quantities of energy difference, vibration frequency, and path length for the linked minimum and transition point. The results are validated with large databases of paths for various potentials, with excellent agreement where the minimum lies in close vicinity of the transition point.

A similar relation is also derived from the cusp catastrophe function for symmetrical paths. Here the non-Morse critical point gives birth to two geometrically equivalent transition points linked to a central minimum or to a central local transition point linked to equivalent peripheral local minima. Such symmetrical critical point triples arise, for example, in simple rearrangements between permutational isomers in clusters of identical atoms.

Wales' application of catastrophe theory, an analytical tool not widely familiar to the scientific community, to energy landscapes is an exciting new development. It is too soon to tell how useful the theory will prove in explaining the complex behavior of such diverse systems as glasses, clusters, and proteins, but an intriguing beginning has been made.

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PERSPECTIVES: CHEMISTRY

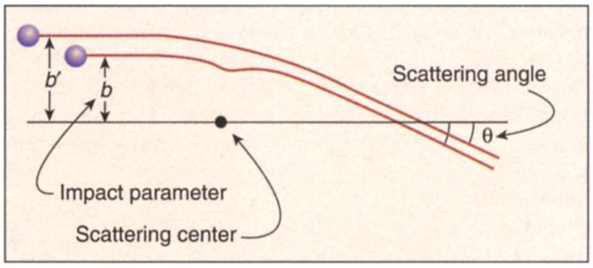
Close Encounters

F. Fleming Crim

For a chemical reaction to occur, molecular collisions must deposit energy in a reactant or bring reactants together such that they can rearrange bonds. Powerful experimental and theoretical techniques are unraveling the details of these encounters, as the report by Lorenz *et al.* (*1*) on page 2063 of this issue illustrates. The authors combine several experimental and computational techniques to measure and analyze the sense of rotation of a molecule after a collision. The study reveals the role of subtle quantum mechanical effects in such encounters.

Today's arsenal of experimental techniques for studying atomic and molecular collisions comprises scattering probes, which observe the direction and speed of molecules after a collision, and spectroscopic probes, which detect the quantum state of the molecules—that is, their particular configuration of energy, spin, momentum, charge, and other quantum properties. In combination, the two techniques yield detailed information about molecular motion during a collision.

In such a combined experiment, a beam of molecules prepared in one or a few quantum states crosses another beam of similarly prepared atoms or molecules. The pressure is low to ensure that each molecule collides at most once, at the point where the beams cross. Collision may result in energy transfer (inelastic scattering) or a reaction (reactive scattering). Some experiments determine the recoil speed and angle of the scattered molecules and infer their total internal energy. Others use spectroscopy to observe the population of individual quantum states, determine the internal energy of a single product state, and identify the molecular motion (such as vibration or rotation) in which this energy resides.



Different paths—same outcome. Two trajectories with different initial conditions (shown here in the center of mass) give the same scattering angle. Attractive forces draw the trajectory with the smaller impact parameter b toward the scattering center until repulsive forces direct it outward, resulting in the scattering angle θ. The trajectory with b' experiences mainly attractive forces, which carry it to the same scattering angle θ. A quantum mechanical particle may sample both paths, producing interferences.

One of the most informative observations in a scattering experiment is the range of angles in which the products appear. This angular distribution reveals a great deal about the interaction of the molecules. For example, a broad, symmetric distribution often signals that the interaction is "sticky"; that is, it proceeds through a complex that rotates many times before it decomposes. In contrast, a narrow, asymmetric distribution indicates an interaction that is much shorter than the rotation time.

One may measure the angular distribution by moving a detector about the intersection region and measuring the intensity of scattered molecules at each angle. Alternatively, laser spectroscopy can provide similar information about the recoil direction and speed of the scattered molecules by viewing the entire distribution (for a single quantum state) at once (*2*, *3*). The first imaging experiments of this kind observed photolysis products (*4*). One of the earliest applications to scattering measured the energy transfer in collisions of Ar atoms with NO molecules (*5*, *6*). This system is the same one that Lorenz *et al.* studied to determine the sense of rotation of scattered NO.

These experimental tools are only part of the machinery required to understand collision dynamics. Modern ab initio electronic structure techniques allow the interaction energy of a system to be calculated in various geometries. These discrete calculations can be knit together into a smooth function that gives the interaction potential for different orientations and separations, often visualized as a potential energy surface. One of the first triumphs of molecular reaction dynamics was the use of the qualitative topology of such a surface to predict energy requirements and disposal in chemical reactions (*7*).

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With the ab initio potential energy surface, one can calculate the trajectories of the interacting molecules using classical equations of motion. This approach provides the first point of comparison with the experiment. However, because classical mechanics does not contain the wave nature of particles, it is inherently unable to reproduce the interference phenomena that are the hallmark of quantum mechanics. Classical trajectories that carry products to the same angle through different paths (see the figure) simply add at the detector, whereas quantum mechanical trajectories interfere, reinforcing at some angles and canceling at others depending on the difference in the path lengths. Only a highly resolved experiment and a comparably detailed quantum mechanical calculation can observe and predict such behavior.

Lorenz *et al.* use all these tools to study the scattering of Ar by NO. They cross a beam of cold NO molecules in their lowest rotational state with a beam of Ar and detect the angle and speed distribution of the scattered NO in different rotational states by ionizing the NO and imaging it onto a detector. The use of circularly polarized light is the crucial addition to their imaging experiment. The interaction of this light with NO depends on the sense of molecular rotation, and the experiment is therefore sensitive to the direction, not just the amount, of rotation.

It seems surprising at first that the experiment should produce a preferred sense of rotation; after all, the impact parameter—the "miss distance" labeled *b* in the figure—and orientation of the molecules are randomly distributed in the crossed molecular beams. Indeed, there can be no preferred sense of rotation for the entire distribution of molecules, but a preferred rotation direction for particular scattering angles and product states is possible. Lorenz *et al.* observe this effect. They find that NO rotates in one direction on one side of the angular distribution and in the other on the opposite side, in agreement with a classical prediction.

The most telling observation, however, is that the sense of rotation oscillates with scattering angle. The observation agrees quantitatively with quantum mechanical calculations using an ab initio potential that includes the attraction between the molecules (*8*, *9*). In contrast, a classical calculation using solely repulsions between the molecules recovers only some features of the scattering.

The study illustrates a new and powerful application of highly resolved experimental techniques and sophisticated theoretical calculations. Similar approaches are possible for reactive collisions, where reactant and product orientation is likely to play an important role. Such studies promise an intimate view of chemistry at the level of individual collisions.

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PERSPECTIVES: PALEOCLIMATE

No Two Latitudes Alike

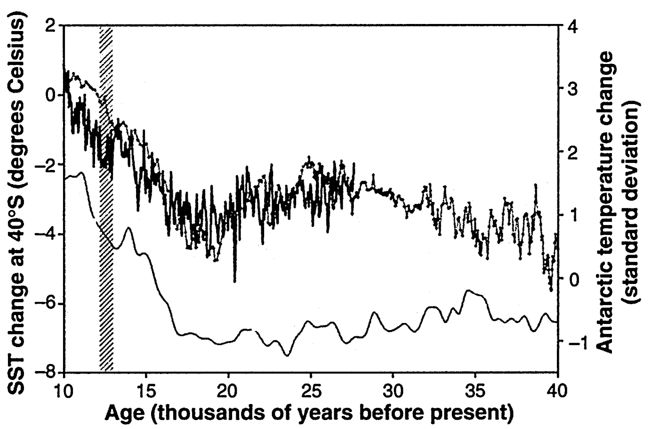
Eric J. Steig

Ice and ocean sediment cores provide a detailed picture of the temporal characteristics of climate over the past 100,000 years. We now know that the slow variations of the ice-age cycles were regularly interrupted by more rapid events, during which mean annual temperature changed by as much as 10° or 20°C in just a few decades (*1*). However, except for the past 600 years (*2*), the spatial pattern of climate change remains virtually unknown because most data come from just a few locations: the Greenland Ice Sheet, the Antarctic Ice Sheet, and the North Atlantic Ocean.

Two reports in this issue help to address this problem by providing records of sea surface temperatures (SSTs) in the mid-latitude oceans of the Southern Hemisphere, a particularly data-poor area. Both studies show that the timing of temperature change in this area is substantially different than in either the North Atlantic or Antarctic. This result will please those that argue that the tropics and mid-latitudes have a larger role to play in climate change than has generally been believed.

The first set of data comes from an ice core from Dome C in East Antarctica. This may seem a surprising location for a record of mid-latitude SSTs. The idea is that deuterium excess—the small difference between oxygen and deuterium isotope ratios—should provide a measure of evaporative conditions at the ocean source of polar moisture. However, researchers have been reluctant to interpret deuterium excess data in terms of SST because other variables, particularly relative humidity, also affect deuterium excess (*3*). On page 2074, Stenni *et al.* (*4*) address this problem in three ways.

First, they note that the modern distributions of humidity and temperature are highly correlated with latitude. This correlation seems to hold through major climate transitions, allowing them to use the isotope data to define a unique set of relations between ice sheet surface temperature and humidity and temperature at the ocean surface. Second, they allow both humidity and SST to vary independently in a simple atmospheric model to place statistical error distributions on the temperature estimates. Third, they show that the sodium concentrations in the ice core record—a proxy for ocean surface wind speed and meridional air mass transport—vary exponentially with the magnitude of the temperature difference between the ocean moisture source and ice sheet. This is the expected relation, indicating that the latitudinal temperature gradient is correctly quantified by the isotopic data.



Temperature change in the Southern Hemisphere. Temperatures are given relative to the average early Holocene temperature. Red line: SSTs from South Atlantic core TN057-21-PC2 at 41°S (*5*). Blue continuous line: Indian Ocean SSTs from Dome C, Antarctica (*4*). Black continuous line: Antarctic surface temperature change at Vostok after correction for moisture-source changes (*8*). Shaded area: Younger Dryas cold period as defined in European and Greenland climate records.

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