not just white noise or filtered white noise, is relevant as a zero-coupling limit in the noise models inescapably leads one to say that certain non-Gaussian fields are relevant as zero-coupling limits in field theory. Of course, such pseudofree quantum field models need not be in conflict with any general principles; for example, asymptotic fields for pseudofree models would be free fields and would most likely have trivial scattering.

Discontinuous perturbations in quantum theory are potentially as relevant as the more familiar continuous perturbations. They deserve study and analysis with an eye toward possible applications in the real world. As we have related, highly suggestive arguments can be put forth that discontinuous perturbations are relevant for nonrenormalizable field thories. It is certainly tempting to believe them, for in one stroke this would explain the grossly unsatisfactory results obtained through conventional perturbation theory as well as provide a suggestion for determining a meaningful solution. Soluble models show that this is the case and make the goal worth pursuing. Techniques need to be devised to discover and recognize the indelible imprints that discontinuous perturbations invariably leave behind—and one hopes for better insight than displayed in Fig. 4!

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Starvation Kinetics

Bond-breaking denied adequate activation by collision can be starved in many ways.

Henry Eyring

Summary. Reactions that take place in shock waves are slow compared to the energy present in the translational degrees of freedom. One explanation for the slow burning in a detonation is that successive surface layers of the solid or liquid must react sequentially. Another mechanism, which can also account for the slowness of reactions in shock waves in gases, is the basis for starvation kinetics: the bond that is breaking must draw its activation energy from a vibrational reservoir in disequilibrium with the translational degrees of freedom of the reacting molecule.

An interesting place to look for fast reactions is in detonations. Shock waves accompanying detonations in solids move through the explosive at some 40 times the 700 miles an hour of sound in air. The shock initiates the decomposition of the explosive, but the rate of decomposition in solids and liquids is slow considering the temperature of the burning explosive. This is sometimes because layers have to be peeled off sequentially from the surface of the burning particles so that the measured rate is the rate of reaction of a molecule in the surface layer divided by the number of molecular layers lying between the surface and the center of the particle. In a liquid, since the reaction starts from the surface of hot gas bubbles and again progresses layer after layer, the rate per molecule must again be divided by the number of layers to be burned through to obtain the measured rate.

Since this same slowness of reaction is reported in shock waves in the gas phase, another mechanism would have to be active in such cases, and if it is, it would also be expected to appear in some solid explosives. Unimolecular reactions become bimolecular when there are not enough activating collisions to keep decomposition at its high-pressure rate (*1*). This is conveniently thought of as one form of starvation kinetics. The bond that is breaking is no longer fed fast enough to be in equilibrium with the translational degrees of freedom around it, but must draw its activation energy from a starving vibrational reservoir with which it equilibrates. However, there are other ways of starving the reservoir besides simply reducing the pressure of molecules colliding with it. One such way is to introduce inefficient transmissions of energy to the reservoir. This inefficiency varies with the type of coupling made in collisions. An obvious way to produce a starvation process is to use a shock wave. In this case the time or intensity of the shock, or both, can produce a starving reservoir in equilibrium with the hidden breaking bond and lead to a slow reaction rate. That such starvation happens must be obvious to every student of the initiation or dying out of detonations in both gases and solids. In fact, starvation kinetics is the name of the game. This process of starvation of shock waves was discussed at some length in my Priestley lecture (*2*).

Starved reaction reservoirs are conveniently made by dumping measured amounts of energy into the reservoirs by all kinds of means. The formation of various degrees of starved reservoir reactions in mass spectra can be devised by regulating the voltage of the ionizing

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electrons and the temperature of the molecules to be ionized or by having the molecules absorb a photon of appropriate energy. Rosenstock *et al.* (*3*) developed the theory for this type of unimolecular decomposition of starved positive ions. Molecular beam experiments provide evidence of such starved reservoir decompositions as random scattering of reaction products. Other examples will come to mind, but I will now discuss further such starved reaction kinetics in shock waves.

Kinetics of Starved Reservoir Reactions

The rate of the reaction in a solid cylinder may be estimated as follows. Since the pressure driving the shock wave comes from momentum transfer and since the escape of this momentum occurs over the whole unconfined surface area of the explosive, lying between the shock wave front and the Chapman-Jouquet surface at a distance a from the front, we expect the velocity of the shock to fall off with the extent of this unconfined escape area. Thus we write for the relative velocity of the shock wave for a cylindrical explosive of diameter d the expression

$$\frac{D}{D^*} = \frac{\pi d^2/4}{\pi d^2/4 + \pi d a \alpha} = \frac{1}{1 + 4a\alpha/d} \approx 1 - 4a\alpha/d$$

We use D to indicate the velocity of the shock wave in a cylinder of diameter d; D^* is the velocity of the shock wave in a cylinder of very large cross section where the area of the cross section is the site of the only important loss of momentum. The reason for the factor α is important. The rate of escape from the side of the explosive is lower per unit area than the rate of escape from the back since it must start at zero at the shock front. Thus α is the average rate of escape per unit area from the side relative to the rate from the back, where the driving pressure has reached its maximum value at the Chapman-Jouquet plane. A rough estimate of α is 1/4, giving us the result

$$\frac{D}{D^*} = 1 - \frac{a}{d} \qquad (1)$$

This is the result Eyring *et al.* (*4*) came to in a detailed investigation many years ago. The observed rate constant, k, is then estimated as approximately

$$k = \frac{D^*}{a} \qquad (2)$$

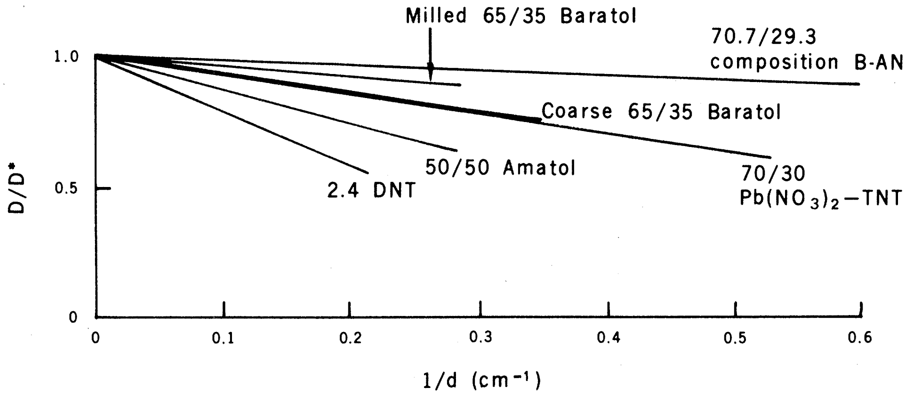


Fig. 1. The slopes of the lines give the value of the reaction zone length, a, in accord with the equation $a = [(D^* - D)/D^*]d$. The value of a is in the neighborhood of 1 cm for all the explosives considered here. Accordingly, the rate constant $k = D^*/a$ is always in the neighborhood of 10^5 or 10^6 for the observed temperatures, near 3000°K.

It is observed that D/D^* is linearly related to $1/d$, for not too small values of d, as required by our explanation. Figure 1 exhibits this expected linearity.

The observed values of k in solid explosives estimated in this way are in the neighborhood of 10^5 to 10^6, far below the value expected if the hidden bonds to be broken were in equilibrium with the hot translational degree of freedom in the shock wave and controlled by the same mechanism. The starved state of the reservoir feeding energy into the hidden bond is understandable. A moment before it was struck by the shock wave it was part of the cold solid explosive. The molecules of explosive are suddenly volatilized relatively cold and, if not decomposed, decompose at the hidden bond, which breaks while equilibrating with a heat-starved reservoir that has barely reached an energy in all its degrees of freedom equal to that required to break the fissile bond unimolecularly.

An appropriate approximate theory is readily formulated. The specific rate constant, k, for two unimolecular reactions in series with rate constants k_2 and k_3 is

$$\frac{1}{k} = \frac{1}{k_2} + \frac{1}{k_3} = \frac{k_2 + k_3}{k_2 k_3} \qquad (3)$$

or

$$k = \frac{k_2 k_3}{k_2 + k_3} \qquad (4)$$

Now for the specific unimolecular rate constant of a reaction in equilibrium with translational degrees of freedom at temperature T we have

$$k_2 = \kappa \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (5)$$

where k, h, and R are Boltzmann's constant, Planck's constant, and the gas constant; the transmission constant κ is ordinarily close to unity; and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (*5*) are the heat and entropy of activation, which can be determined by studying the rate of decomposition at low temperatures, where the bond to be broken stays in equilibrium with the translational degrees of freedom.

For a bond whose dissociation energy is $\mathcal{D}$ in equilibrium with a reservoir of s oscillators there is an expression for the specific rate of decomposition which we will now calculate. The probability p_s that such a reservoir will have an energy $\mathcal{D}$ or more in s degrees of freedom is

$$p_s = \sum_{i=0}^{s-1} \frac{1}{i!}\left(\frac{\mathcal{D}}{RT}\right)^i e^{-\mathcal{D}/RT} \qquad (6)$$

The probability p_1 that a degree of freedom in equilibrium with this heat reservoir will have an energy $\mathcal{D}$ or more is accordingly

$$p_1 = e^{-\mathcal{D}/\gamma} \qquad (7)$$

where γ is the average energy of an oscillator in the reservoir. Accordingly, the rate of decomposition of a bond whose energy of decomposition is $\mathcal{D}$ is approximately

$$k_3 = \frac{kT}{h} p_1 p_s = \frac{kT}{h} e^{-\mathcal{D}/\gamma} \sum_{i=0}^{s-1} \frac{1}{i!}\left(\frac{\mathcal{D}}{RT}\right)^i e^{-\mathcal{D}/RT} \qquad (8)$$

Obviously, decomposition of the bond is impossible until the energy in the $s + 1$ degrees of freedom of the reservoir and the reacting bond exceeds $\mathcal{D}$, and it should be proceeding at a reasonable starved rate when the energy in the reservoir itself has reached $\mathcal{D}$, in which case $\gamma = \mathcal{D}/s$ and k_3 becomes

$$k_3 = \frac{kT}{h} e^{-s} \sum_{i=0}^{s-1} \frac{1}{i!}\left(\frac{\mathcal{D}}{RT}\right)^i e^{-\mathcal{D}/RT} \qquad (9)$$

Table 1. Data for the specific reaction rate k_z.

Explosive	$\Delta S^\ddagger$ (cal mole^{-1}deg^{-1})	$\mathcal{D}$ (kcal mole^{-1})	Range of temperatures (°K)	Reference
Ammonium nitrate	−5.33	37.3	490–540	(*11*)
Ethylenediaminedinitrate (EDNA)	−10.45	30.0	417–437	(*11*)
Hydrazine mononitrate	−5.53	37.2	412–493	(*11*)
Tetryl	8.88	37.4	484–533	(*12*)
TNT	−5.86	42.3	510–550	(*11*)
TNT	−9.63	33.3	548–583	(*10*)

Table 2. Values of k for a number of solid explosives. The D^* values are from (*7*).

Explosive	a (cm)	D^* (cm/sec)	k (sec^{-1})
70.7/29.3 Composition B-AN	0.25	7.5×10^5	3.04×10^6
70/30 $Pb(NO_3)_2$-TNT	0.70	6.09×10^5	8.70×10^5
Milled 65/35 Baratol	0.40	5.64×10^5	1.41×10^6
2,4-DNT	2.12	4.20×10^5	1.98×10^5
Coarse 65/35 Baratol	0.75	5.63×10^5	7.51×10^5
50/50 Amatol	1.25	6.93×10^5	5.54×10^5

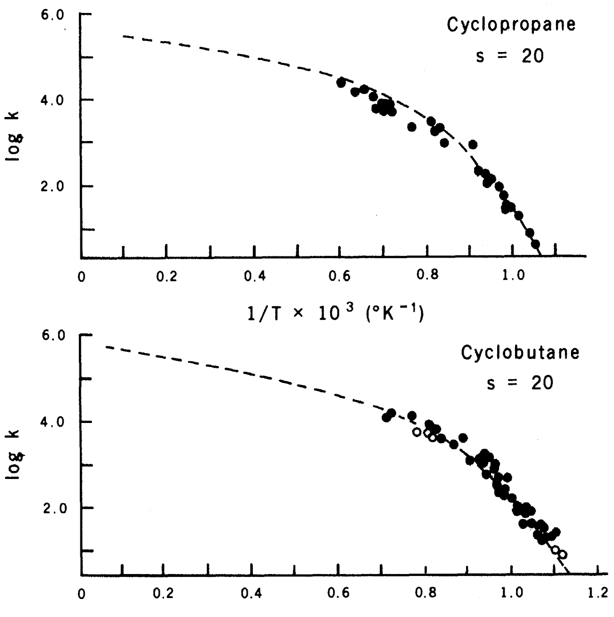
Equation 4 was applied by Eyring and Leu (*6*) to the experimental results of Barnard and co-workers (*7, 8*) and Bradley and Freud (*9*) for the shock tube detonations of cyclopropane and cyclobutane, which we interpreted as starvation kinetics. The results are shown in Fig. 2.

It is interesting that the value $s = 20$ for the number of oscillators in the reservoir is the expected number for propane, whereas in cyclobutane one might expect as many as nine more if they were all in good communication with the breaking bond. This lack of communication of part of the bonds is also observed in starvation reactions at low pressures. It is noteworthy that the extrapolated high-temperature limit for k is 10^5 to 10^6. This is far below the value that would be expected if the breaking bond were in equilibrium with the translational degrees of freedom corresponding to k_2, for which $\Delta S^\ddagger$ and $\mathcal{D}$ are given in Table 1. This same low value for k at high translational temperatures is found for many solid explosives, as may be seen in Table 2 and Fig. 3.

Discussion

This theory of starvation kinetics is suggestive of how detonations may be modulated advantageously. Thus, in a shaped charge shock waves are not only focused but, on reflection, pass over unreacted material and in so doing speed up decomposition in the hollowed-out space, with an accompanying enhanced spewing out of decomposition products. This reflection from the sides of the hollowed-out shaped charge can bring up the pressure and therefore the velocity near the axis of the shock wave to a value near that for a charge of infinite diameter, and yet the intensified shock wave has only to push out a plug of small cross section in the material to be penetrated. The result is the familiar intense penetrating power obtained with the Munro effect. A shock wave is highly temperature-sensitive at temperatures below that at which starvation kinetics takes over. As a result, the shock wave will behave very erratically if there are random holes or random changes in density in the explosive. A shock wave will ignite an explosive or die out depending on whether it is losing energy to vibrational degrees of freedom slower or faster than it is gaining energy from decomposition. To quantitiatively handle such problems it is essential to take into account shifts between ordinary kinetics and starvation kinetics.

Here again the observed rates are all



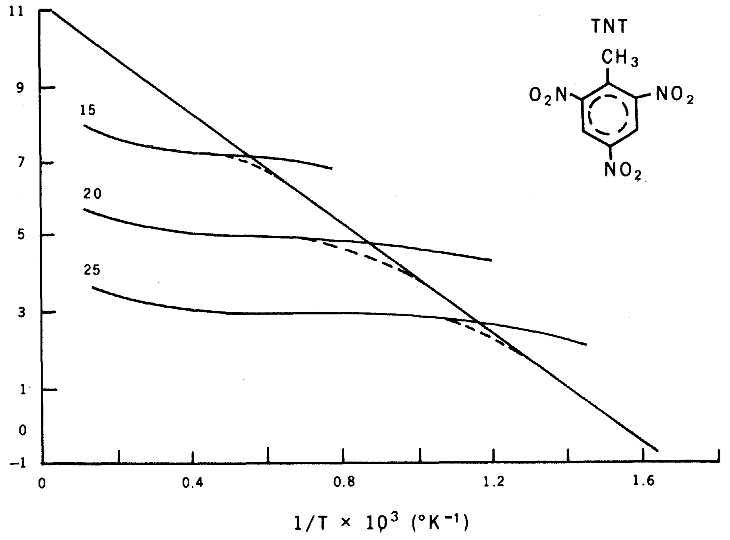


Fig. 2 (left). Theoretical log k, where k is given by Eq. 4, plotted against $1/T$ (dashed lines) for the decomposition of cyclopropane and cyclobutane. The circles are the experimental values (*1*). Here k_2 is given by Eq. 5 and k_3 by Eq. 9. Also $\Delta H^\ddagger = \mathcal{D}$, the dissociation energy, and $s = 20$ is the number of vibrational degrees of freedom feeding the reaction coordinate. Fig. 3 (right). Here we see that a reservoir with s oscillators, where $s = 20$ and k is given by Eq. 4, gives the observed specific rate between 10^5 and 10^6 (see values of k in Table 2). Here the low-temperature observed rate of Robertson (*10*) is used.

Here again the observed rates are all calculated by the procedure used for cyclopropane and cyclobutane with various values of the number of effective degrees of freedom, s, in the reservoir. The best agreement between the calculated values of k in Fig. 2 and the observed values in Table 2 is obtained for a reservoir with about 20 degrees of freedom. For Fig. 3 the experimental data of Robertson (*10*) were used to calculate k. The same general conclusions are reached if the experimental data of Cook and Abegg (*11*) are used.

The theory that the observed slow rate of burning in a detonation results from sequential burning of successive surface layers of a solid or liquid and the theory developed here that slow reaction arises from disequilibrium between translational and vibrational degrees of freedom of the reacting molecule both invoke the same rate-determining step—that is, slow heat transport from translational to vibrational degrees of freedom. Slow diffusion of reactants to the site of reaction is another kind of starvation kinetics frequently encountered. We can only deal appropriately with such delayed reaction rates as we recognize and sort out the exact cause. Clearly a change in the temperature dependence of reaction provides symptomatic although not conclusive evidence of the nature of the change in mechanism. Experiments designed to establish the exact cause of changes in mechanism are needed and will be particularly valuable.

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A Disaster in the Environmental Movement

The National Environmental Policy Act has wasted environmentalists' resources on processing papers.

Sally K. Fairfax

Critics of the National Environmental Policy Act of 1969 (NEPA) are relatively rare, and they fall into two categories: those whom it affects adversely and those who think it is interpreted too narrowly. The complaints of those whom NEPA affects adversely are frequently dismissed as self-interested or as motivated by a desire to continue their activities without consideration of environmental costs (*1–3*). Those who think NEPA's mandate is being given too cramped an interpretation praise NEPA generally but have reservations which are reflected in calls for vigorous application or for more expansive interpretation of all parts of NEPA (or both). While they believe that NEPA brought a new day in responsible agency decision-making, they see that it has not solved all of our environmental problems (*4–13*). In this article I seek to establish a third type of criticism: that, far from being a salubrious process in need of further elaboration and refinement, NEPA has been a disaster for the environmental movement and for the quest for environmental quality.

My argument is made by countering a considerable body of opinion praising what is called the "NEPA process" (*4–17*). The general opinion is that NEPA has improved agency decision-making processes by altering internal agency deliberations and by opening them to public scrutiny and participation. I suggest that NEPA does not constitute a new approach to administrative reform and is actually a poor vehicle for a reformation of agency decision-making. Litigation under NEPA and preoccupation with the NEPA process truncated preexisting and potentially significant developments in the definition of agency responsibility for environmental protection and in citizen involvement in agency deliberative processes. It turned environmentalists' efforts away from questioning and redefining agencies' powers and responsibilities and focused them instead on analyzing documents. This preoccupation has led to a misallocation of the environmental movement's resources.

The initial response of environmentalists to the passage of NEPA is now described as euphoric (*4*). In fact, the initial response was limited and skeptical. Very little appeared in the popular press at all. What did appear in the environmentalist publications can only be described as reserved (*5, 14, 15*). The initial reaction displayed in the legal and professional journals emphasized the limitations of another round of procedural review. Much of the discussion focused on the Council on Environmental Quality (CEQ) (*16, 17*). The "action forcing provisions" requiring impact statements received relatively little attention (*17, 18*). In general, the initial response of agencies to NEPA was minimal. Many agencies believed that the act did not affect them because their activities already reflected its policy goals (*19*). Thus, far from being greeted with a chorus of praise, NEPA aroused surprisingly little interest, and much of that was focused

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