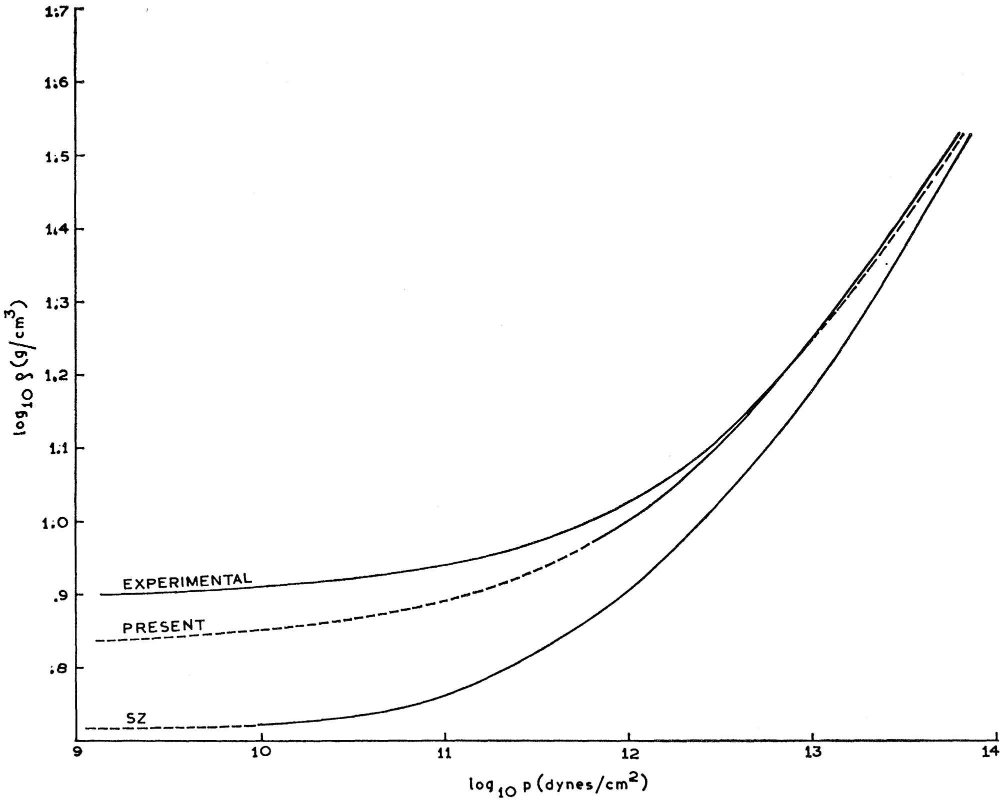

FIG. 1. Density versus pressure curve for $_{26}$Fe. The experimental curve represents the reduced shock-wave data (taken from Ref. 1). The curve SZ is based on TFD plus average correlation corrections (Ref. 1). The present curve is based on TFD plus the quantum and the average correlation corrections.

The matter density is given by

$$\rho = 1.664[AZ/(ZV)]\ \mathrm{g/cm^3}, \qquad (6)$$

where A is the atomic mass in physical atomic-mass units.

Results for the equation of state of $_{26}$Fe are shown in Fig. 1 along with the experimental data (taken from SZ) and the results of SZ. From the figure we see that the simple procedure outlined in this note improves the agreement with experimental data.

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Reaction-Rate Kinetics and Distribution of Activation Energies

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In the problem of the determination of the characteristics of reaction-rate kinetics through the analysis of isothermal (or isochronal) data, we show that (1) it is impossible to determine both the order of reaction and, concurrently, the distribution of activation energies, and that (2) without prior knowledge of one of these—either the order of the reaction or the distribution of activation energies—the other cannot be determined in a unique manner.

A SYSTEMATIC study of the kinetics of processes distributed in activation energy was made by Primak,[1] who also gave an impressive list of fields in physics where this concept has been applied. We follow, in general, the notation of Primak to write the kinetic equation

$$-\frac{dq}{dt} = \lambda q^{n}, \qquad (1)$$

where q is the concentration of the reactant, t is the

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[1] W. Primak, Phys. Rev. **100**, 1677 (1955).

time, λ is a constant, and n is the order of reaction. For a given n, Eq. (1) can be integrated at once to analyze isothermal data. Thus,

$$\begin{aligned} q &= q_0[1+(n-1)q_0^{n-1}\lambda t]^{1/(1-n)} \quad \text{for} \quad n>1 \\ &= q_0 e^{-\lambda t} \quad \text{for} \quad n=1. \end{aligned} \tag{2}$$

In reaction processes, the rate constant λ is usually given by the Arrhenius expression

$$\lambda=\lambda_0 e^{-E/kT}, \tag{3}$$

where E is the activation energy and kT is the product of Boltzmann's constant and the absolute temperature. Therefore, the reaction kinetics are characterized by Eqs. (2) and (3).

Now assume that there exists a distribution of activation energies, so that q_0 and λ are in fact dependent on such a distribution. We then ask the followlng question: What are the distribution functions implicit in q_0 and λ which would give the same functional form in time and temperature as given for q in Eqs. (2) and (3), i.e., with a single governing activation energy? The answer is that q_0 and λ must be Dirac δ functions, i.e., of the form $A\delta(E-E_0)$, where A is an unspecified parameter and E_0 is a singular value; in other words, q_0 and λ have null distributions in E. The proof is based on the definition and the uniqueness of the δ function.

In a recent work on the annealing in gold after electron radiation,[2] analysis was made to determine the order of kinetics (it was found $n=2$) as well as to establish a continuous spectrum of distribution of E in q_0. Our mathematical argument shows this analysis is not self-consistent.

Next, we ask the following question: Can one establish the form of a distribution in activation energies based on isothermal (or isochronal) data without a prior knowledge of the order or reaction, and vice versa? The answer is negative.

First, consider the following example: Suppose experimental data are generated by Eq. (2) with $n=2$, but somehow we attempt to analyze the data in terms of a first-order kinetics ($n=1$) with a distribution of activation energies. We have

$$(1+q_0\lambda t)^{-1}=\sum_k a_k e^{-\lambda_k t}. \tag{4}$$

Formally, we can determine the expansion coefficient a_k and the exponential parameter λ_k from the system of equations

$$(q_0\lambda)^j j!=\sum_k a_k \lambda_k^j. \tag{5}$$

Equation (5) does not determine uniquely both a_k and λ_k because there are two times more unknowns than the algebraic equations. Therefore, in fact, we have extra free parameters to choose and we have j values of either a_k or λ_k; each has its own "activation energy." Therefore, either a_k or λ_k can be used to generate a spectrum of activation energies; however, this was *based on a false analysis.*

The above example is based on the preassignment of n. Now, if we leave n free, and if we represent the right side of Eq. (1) by a general function $f(q)$, we only impose a condition that $f(q)$ is meromorphic[3] with as many zeros as we require, then Eq. (1) can be integrated and we have

$$\prod_k (q-q_k)^{\mu_k}=\prod_k (q_0-q_k)^{\mu_k} e^{-\lambda t}, \tag{6}$$

where q_k are zeros of $f(q)$ and μ_k the Riemann residues of f^{-1}. [The expression in parenthesis of Eq. (6) should be q_k-q if $q<q_k$.] Since we have not specified *a priori* the number of n, Eq. (6), in principle, could fit any experimental isothermal or isochronal data, with any desired degree of accuracy, with a *single* λ, i.e., a *single activation energy.*

Therefore, unless there is other physical evidence, as emphasized by Primak himself,[1] it seems there is no mathematical base to establish the activation-energy spectrum, as advocated in the recent literature.[2,4]

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[2] C. Lee and J. S. Koehler, Phys. Rev. **176**, 813 (1968).

[3] E. C. Titchmarsh, *Theory of Functions* (Oxford University Press, London, 1932), p. 110.

[4] Some other examples are: R. M. Kimmel and D. R. Uhlman, Phys. Chem. Glass **10**, 12 (1969); V. Danchenko, U. D. Desai, and S. Brashears, J. Appl. Phys. **39**, 2417 (1968).