occur in relation to equation (2.36) and (2.39) of Schwinger II.

It may be argued that ordinary space-time is as good as (k) space. But the occurrence of new particles appears more directly in the latter on account of the connection with energy and momentum. The effect is as though "elementary particles" had a size, as has been brought out by Heisenberg (*5*).

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Nonclassical Reaction Kinetics

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Barrier leakage was early invoked by Gamow and by Condon and Gurney to explain nuclear decomposition. For particles of mass m, position X, and energy E_i in the ith state, moving on a potential energy surface $V(X)$, the specific reaction velocity, v, (or frequency of passing a smooth energy barrier ($E_i < V$) which occupies the region ($X_1 \leqq X \leqq X_2$)) may be written:

$$v = \sum_i n_1\nu_1\gamma_1 = 4\sum_i n_i\nu_i \exp\left(-\frac{2\sqrt{2m}}{h}\int_{X_{1i}}^{X_{2i}}\sqrt{V(X)-E_i}\,dX\right), \qquad (1)$$

where n_i, ν_i, and γ_i are the fractional population of the ith level, the frequency of vibration normal to the reaction barrier, and the probability of barrier penetration per encounter, respectively. Because of the flatness of barriers in ordinary chemical reactions, leakage is usually negligible in comparison to the surmounting of barriers. The inversion of the ammonia pyramid is one of a small group of interesting exceptions that are reasonably well understood.

Hardness, electrical resistivity, and magnetism of metals, when treated as rate processes, provide added examples of nonclassical kinetics. Application of the classical expression for the net specific rate k'_{net} of surmounting barriers

$$k'_{\text{net}} = \frac{2\kappa kT}{h}\exp\left(-\frac{\Delta F^{\ddagger}}{RT}\right)\sin h\frac{V\cdot\sigma}{2kT} \qquad (2)$$

to plastic flow of metals by Fredrickson and Eyring (*1*) and Kauzmann (*2*) led to a free energy of activation $\Delta F^{\ddagger}$ proportional to the temperature (a pure entropy) and $\frac{V_h}{2kT}$ independent of the temperature. V_h, with the dimensions of volume, is the area of the slipping unit in the plane of slip times the mean distance traveled per slip. That V_h should be proportional to the temperature is not impossible, but scarcely to be anticipated (*3*).

It seems more natural to replace the classical equation (2) for plastic flow by the appropriate extension (1), from which the observed temperature effect follows easily. In this case, the effective potential $V(X)$ is reduced at each point along the barrier by a small amount $a\sigma$, against motion of the particles in the direction to relax the stress σ; and is raised by a similar amount against return to the initial state, once the barrier has been passed. This is to be understood in terms of the distortion of the average electrostatic field by a relative displacement of the mean positions of atomic kernels. Expanding the radical in equation (1) to the first order in powers of $a\sigma$ (the correction to V) and replacing the sum by a single "average" term, we obtain for the excess velocity in the direction to relieve stress over that of return

$$v_{\text{net}} = 8\bar{\nu}\exp(-\bar{g}\overline{m}p)\sin h(\bar{b}\overline{m}p\sigma), \qquad (3)$$

where

$$\bar{g} = \frac{2\sqrt{2m}}{\hbar}\int_{X_{1i}}^{X_{2i}}\sqrt{V-E_i}\,dX, \quad \bar{b} = \frac{\sqrt{2m}}{\hbar}\int_{X_{1i}}^{X_{2i}}\frac{a\,dX}{\sqrt{V-E_i}},$$

and $\overline{m}$ and p will be discussed shortly.

Equation (3) must be interpreted as follows: Crystal geometry permits slip only through the cooperation of $\overline{m}$ neighboring atoms. At moderate temperatures these atoms may be treated as independent oscillators, as in the Einstein theory of specific heats. $\bar{\nu}$ is the effective frequency of vibration of the normal mode along the slip plane. These electrons must each penetrate the electrostatic barriers separating initial and final configurations if slip is to occur. For independent atom vibrations, normal to the slip plane factors relating to the individual probabilities of penetration must be raised to a power $\overline{m}p$, where p is the average number of exterior electrons on each atom. The electronic integrals are to be averaged over the atomic vibrations, where the energies and limits of integration depend upon atomic coordinates. Except for temperature dependence, equation (3) has the same behavior as (1), the validity of which has already been studied.

This formalism also makes clear the effect of large amounts of alloy elements on plasticity. Since the local regions of slip are considerably less orderly than the perfect crystal, in the first approximation atomic interactions can be considered to take place between pairs of neighboring atoms. If x is the atomic fraction of constituent A, and $(1-x)$ that of B, then evidently for alloys $p\bar{g}$ takes the form

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[1] The authors are indebted to ONR for support of this research activity. (Because the authors failed to receive proofs of this article before the issue wento press, any necessary corrections will be printed later.—Eds.)

$$P_{AA}\bar{g}_{AA}x^2 + 2P_{AB}\bar{g}_{AB}x(1-x) + P_{BB}\bar{g}_{BB}(1-x)^2$$

where the constants are appropriate to reactions between the various pairs of species. (In general, higher terms in x are necessary in $p\bar{g}$, to account for interactions with all neighbors, or where phase transformations are involved.) As a criterion of hardness that will show the same dependence upon alloy composition as Brinell number, we may take that value of stress necessary to produce a certain standard velocity of deformation $\frac{ds}{dt} = \lambda v_{\text{net}}$; for which velocity we choose the convenient value $4\lambda\bar{v}$, where λ represents the average deformation occurring with each elementary slip process. For the high local stresses associated with Brinell impressions, we replace $\sin hp\overline{bm}\sigma$ by ½ exp $p\overline{bm}\sigma$ in equation (3) and obtain

$$\sigma = \frac{P_{AA}\bar{g}_{AA} + P_{BB}\bar{g}_{BB} - 2P_{AB}\bar{g}_{AB}}{\bar{b}}x^2 + 2 \times \frac{P_{AB}\bar{g}_{AB} - P_{BB}\bar{g}_{BB}}{\bar{b}}x + \frac{P_{BB}\bar{g}_{BB}}{\bar{b}} \quad (4)$$

where σ is taken to be a linear function of Brinell number.

The intimate similarity between this mechanism of plastic flow and that of electrical conductivity cannot be overlooked. In a very simple model for the latter, current is proportional to the average frequency with which electrons pass the electrostatic barriers offered by quasi-crystalline fields in the regions between adjacent atoms. Neglecting slight geometrical considerations, plastic slip of one atom past another constitutes a "relative current" of this same type; accelerating voltage being provided by the fields of displaced atomic kernels in one case, and externally applied in the other. It is to be expected that equation (3) may, therefore, also give a qualitative account of rate of current flow if the relative energy of barrier lowering, $\overline{m}bp\sigma$ in the plastic flow case, be replaced by $eb'\varepsilon$ where e and ε represent the electronic charge and applied field, and b' is a constant related to $\bar{b}$. Since the applied fields are small in comparison to those atomic fields encountered in plastic flow, the sin$h$ factor in (3) may now be expanded, as well as the exponential factor. Absorbing the $\overline{mp}$'s into the g's, we get for the resistivity R of an alloy,

$$R = \frac{\varepsilon}{J} = \frac{(g'_{AA} + g'_{BB} - 2g'_{AB})x^2 + 2(g'_{AB} - g'_{BB})x + g'_{BB} + 1}{8Ne^2l\nu'b'}, \quad (5)$$

where N is the effective density of electrons, l the mean path length between barrier collisions, and the primed constants are related to those unprimed, above. Temperature dependence arises in the integration of parameters.

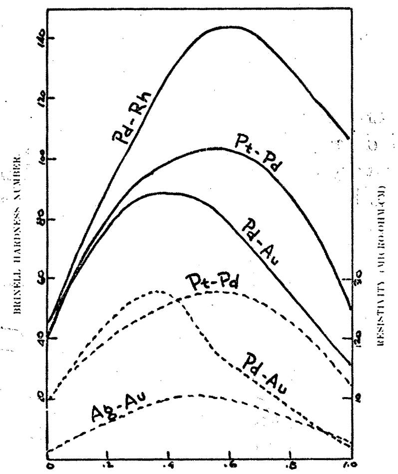

FIG. 1 (*3*).

In Fig. 1 is sketched the experimental variation of Brinell hardness with composition (solid lines) for some binary systems of similar elements, and of resistivity (dashed lines), (all taken from R. F. Vines (*4*) except Ag-Au curve, from Mott and Jones). The pure states of the first-mentioned elements are on the left in the diagram. The parabolic character predicted by equations (4) and (5) is evident, as well as the similarity of hardness and resistivity curves for the systems Pt–Pd and Pd–Au.

Magnetism, another phenomenon to which the "relative current" principle may be applied, will be treated elsewhere.

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Quantum-Theoretical Densities of Solids at Extreme Compression

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In no way, perhaps, is a new theory more apt to show its power and range than in extrapolation and prediction related to phenomena previously inaccessible. One example of this, applied to quantum mechanics, is the computation of the behavior of matter under extreme pressures and temperatures, particularly the well-known applications to the interior of the stars. A less well-known example is furnished by similar applications to the interior of the earth.

In recent years, Bridgman (*1*) has succeeded in determining the densities and compressibilities of a large number of elements and compounds up to a pressure of 100,000 atmospheres. All his values for elements and a few selected ones for compounds are plotted on the left-hand side of Figs. 1–3 in a double-