

ing value for similar mice bearing spontaneous mammary cancers was 17 milligram. The extra B₁₂ was thought to have arisen from synthesis by the tumor. Other explanations were also considered. A transplanted strain of these cancers was found to give similar evidence for vitamin B₁₂ synthesis. A second transplanted strain showed no evidence for such synthesis but, instead, was demonstrated to bring about active destruction of the vitamin in vitro. Several individual spontaneous mammary cancers were likewise shown to destroy this vitamin, but not so actively as did the one transplanted strain. This destruction was shown to be different from mere combination of a protein with the vitamin, such as is known to occur in gastric juice.

* With the technical assistance of V. Armbrust and G. Schaffner.

¹ D. W. Woolley, these PROCEEDINGS, **39**, 6, 1953.

² D. W. Woolley, *J. Exptl. Med.*, **93**, 13, 1951.

³ D. W. Woolley, *Proc. Second Intern. Biochem. Congr.* (Paris), July, 1952.

⁴ D. W. Woolley, *Cancer Research*, **13**, 327, 1953.

⁵ D. W. Woolley and G. Schaffner, *Cancer Research*, **14**, 802, 1954.

⁶ L. M. Zucker and T. F. Zucker, *Arch. Biochem.*, **16**, 115, 1948.

⁷ A. M. Hartman, L. P. Dryden, and C. A. Cary, *Arch. Biochem.*, **23**, 165, 1949.

⁸ S. H. Hutner, L. Provasoli, and J. Filfus, *Ann. N.Y. Acad. Sci.*, **56**, 852, 1953; F. W. Barber, D. L. Baile, C. B. Troescher, and C. N. Huhtanen, *Ann. N.Y. Acad. Sci.*, **56**, 863, 1953.

⁹ J. E. Ford, *Brit. J. Nutrition*, **6**, 324, 1952.

¹⁰ B. D. Davis and E. S. Mingioli, *J. Bacteriol.*, **60**, 17, 1950.

¹¹ H. E. Scheid, M. M. Andrews, and B. S. Schweigert, *J. Nutrition*, **47**, 601, 1952.

¹² This, in fact, was used as an argument against the idea that the apparent synthesis in the spontaneously tumorous animals was due to bacterial infection or necrosis of tissues.

A GENERALIZED THEORY OF PLASTICITY INVOLVING THE VIRIAL THEOREM*

BY HENRY EYRING AND TAIKYUE REE

UNIVERSITY OF UTAH

Communicated December 22, 1954

The theory of plastic deformation proceeds by considering a series of relative displacements of patches lying on the two sides of each shear surface. Displacements along such shear surfaces occur as relaxations obeying a generalized absolute reaction rate equation. A general statistical formulation has been achieved which fits the usual cases of shear. Application of these results to various types of cases will appear elsewhere. A generalization of the absolute reaction rate equation is also presented.

A calculation of the probability, P_i , that a molecular system, A , will have the total energy, ϵ_i , distributed in some unique way among its degrees of freedom, where A is in equilibrium with a large number of oscillators whose mean available energy is γ , yields the result¹

$$P_i = C e^{-(\epsilon_i/\gamma)}. \quad (1)$$

The appropriate value to take for γ depends on the circumstances. There are a variety of important cases involving different types of degrees of freedom.

Case I: For degrees of freedom at equilibrium γ will have the value kT , where T is the temperature of the system as a whole.

Case II: If some irreversible rate process is in operation, it may be that for certain degrees of freedom the local statistical γ may be well approximated by kT_l , where the subscript l indicates the local value. Thus the appropriate T_l may be considerably different from the over-all measured temperature T .

Case III: If we have a frozen-in equilibrium with respect to certain degrees of freedom, it may be convenient to write for them $\gamma_f = kT_f$. Here T_f is the temperature at which the equilibrium was frozen in and may have nothing to do with the ambient temperature.

Case IV: If, after an equilibrium is frozen in, certain components are arbitrarily removed or modified, we may be obliged to give up the frozen-in equilibrium concept and replace it by a detailed accounting for the individual species present.

Case V: In the same way it may be that there is no local temperature, T_l , which, combined with equilibrium theory, will properly describe all the relative concentrations in certain groups of states. In this case, the group of states must be broken into subgroups until such a local temperature can be properly applied to each of the subgroups. This final subdividing into equilibrated subgroups may end with a single quantum state in a subgroup.

Now if, beginning with equation (1), we go through the usual quasi-equilibrium derivation of the specific rate constant, k' , we obtain

$$k' = \frac{\kappa \gamma_0}{h} e^{-\sum_{i=1}^S (\Delta F_i^\ddagger / \gamma_i)} \quad (2)$$

Here γ_0 is the mean available energy of those oscillators equilibrating with the translational degree of freedom corresponding to crossing the potential barrier, and γ_i is the same mean available energy of those oscillators equilibrating with the i th group of activated complex degrees of freedom requiring the activation free energy ΔF_i^\ddagger . If there are classical degrees of freedom equilibrating with all the degrees of freedom of the activated complex, each γ can be replaced by kT , and we obtain the familiar rate expression,

$$k' = \kappa \frac{kT}{h} e^{-(\Delta F^\ddagger / RT)} \quad (3)$$

Various kinds of incomplete equilibration of activated complex degrees of freedom are observed in plastic flow. Consider that shear occurs along sets of parallel planes. The distance between these planes is indicated by the symbol λ_f . The shear force per unit area is indicated by f . A patch of atoms or molecules whose cross-sectional area is $\lambda_2 \lambda_3$ shift or jump as a unit on either side of the shear plane. We obtain, then, for the rate of shear \dot{S} , when the system is in equilibrium with an external temperature T , the expression^{2, 3}

$$\dot{S} = \frac{\lambda}{\lambda_1} k' 2 \sinh \frac{f \lambda_2 \lambda_3 \lambda}{2kT} = \frac{\lambda}{\lambda_1} \kappa \frac{kT}{h} \exp \left\{ -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \right\} 2 \sinh \frac{f \lambda_2 \lambda_3 \lambda}{2kT}. \quad (4)$$

Here k' is the frequency of displacement of the flow patch per second in the forward and in the backward flow direction when $f = 0$. The distance the patch moves per jump is λ .

The generalized equation when local degrees of freedom fix γ becomes

$$\dot{S} = \frac{\lambda}{\lambda_1} \frac{\kappa \gamma_0}{h} \exp \left\{ \sum_{i=1}^s \frac{\Delta F_i^\ddagger}{\gamma_i} - \frac{\Delta F_s^\ddagger}{\gamma_s} \right\} 2 \sinh \frac{\lambda_2 \lambda_3 \lambda f}{2 \gamma_s}. \quad (5)$$

Equation (5) reduces to equation (4) when $\gamma_0 = \gamma_i = \gamma_s = kT$. When this is not true, the problem remains as to the appropriate values to take for the γ 's.

The Simple Virial Theorem Applied to Viscous Flow.—Consider the usual simple equation

$$\frac{d}{dt}(m\dot{x}) \equiv m\ddot{x} + m\dot{x}^2. \quad (6)$$

Here m , x , \dot{x} , and \ddot{x} are the mass, distance, velocity, and acceleration, respectively, associated with a given degree of freedom. If both sides of identity (6) are integrated from the initial time t_i to some final time t_f , there is obtained the result

$$(m\dot{x})_{t_f} - (m\dot{x})_{t_i} = (\overline{m\ddot{x}} + m\dot{x}^2)(t_f - t_i) \quad (7)$$

or

$$\frac{1}{t_f - t_i} \{ (m\dot{x})_{t_f} - (m\dot{x})_{t_i} \} = \overline{m\ddot{x}} + m\dot{x}^2 = 0. \quad (8)$$

The final zero value follows from looking at the material to the left of the first equality in equation (8). This must be zero, since the difference inside the braces fluctuates about zero, whereas $1/(t_f - t_i)$ approaches zero for averages over long time intervals. Since $m\ddot{x} = X$, where X is the force in the x direction, we write the usual virial expression⁴

$$\overline{Xx} + \overline{m\dot{x}^2} = 0. \quad (9)$$

Here the average is over a very long time. If equation (9) be applied to the reaction co-ordinate for plastic flow, the following identifications can be made:

$$X = f_0 \lambda_2 \lambda_3 \quad (10)$$

and

$$x = g\lambda, \quad (11)$$

where g is the ratio of the length of free vibration, x , of the flowing patch whose area is $\lambda_2 \lambda_3$ to the distance jumped, λ . Thus g should approximate the ratio of sound velocity in the solid to that in the gas—a value in the neighborhood of 7. Here f_0 is the local microstress to be distinguished from the over-all macrostress, f . Further,

$$\overline{m\dot{x}^2} = \gamma_s. \quad (12)$$

We now define ΔF_s^\ddagger as the mean work required to displace unit area along the slip plane a distance $\lambda/2$. Whence the free energy, ΔF_s^\ddagger , to move the patch of area $\lambda_2 \lambda_3$ the distance $\lambda/2$, i.e., to the top of the potential barrier, is

$$\Delta F_s^\ddagger = \Delta F_s^\ddagger \lambda_2 \lambda_3. \quad (13)$$

Combining formulas (9), (10), (11), and (12) yields

$$f_0 \lambda_2 \lambda_3 g \lambda = \gamma_s. \quad (14)$$

Substituting equations (13) and (14) in equation (5) gives

$$\dot{S} = \frac{\lambda}{\lambda_1} \kappa \frac{\gamma_0}{h} \exp \left\{ - \sum_{i=1}^{s-1} \frac{\Delta F_i^\ddagger}{\gamma_i} - \frac{\Delta F_\sigma^\ddagger}{f_0 \lambda g} \right\} 2 \sinh \frac{f}{2gf_0}. \quad (15)$$

As far as the available evidence indicates, it is usually satisfactory to write $\gamma_0 = kT$. However, to the approximation that γ_0 can be identified with the average energy of an oscillator, we have

$$\frac{\gamma_0}{h} = \frac{1}{h} \left(\frac{1}{2} h\nu + \frac{h\nu}{e^{\frac{h\nu}{hT}} - 1} \right) = \nu \left[\frac{1}{2} + \left(e^{\frac{h\nu}{kT}} - 1 \right)^{-1} \right]. \quad (16)$$

at low temperatures this has the value $1/2 \gamma$ and at high temperatures the usual value, kT/h . Rate processes involving electrons and He^{II} seem at least in qualitative accord with the low-temperature form of equation (16), since there is no evidence that processes cease at absolute zero in the way indicated by the factor kT/h . Because of quantum effects at low temperatures, the transmission coefficient, κ , including barrier leakage, will be important, and $K\gamma_0/h$ will be best treated as a unit. Finally, we can write

$$\sum_{i=1}^{s-1} \frac{\Delta F_i^\ddagger}{\gamma_i} = \frac{\Delta F_f^\ddagger}{RT_f} + \frac{\Delta F_e^\ddagger}{RT}. \quad (17)$$

Here ΔF_f^\ddagger is the free energy of activation for these degrees of freedom when they were frozen in at T_f , while the ΔF_e^\ddagger is the free energy of activation for the degrees of freedom which are in equilibrium under the conditions of the experiment.

This leads us to the general equation for shear rate,

$$\dot{S} = \frac{\lambda}{\lambda_1} \kappa \frac{kT}{h} \exp \left\{ - \frac{\Delta F_f^\ddagger}{RT_f} - \frac{\Delta F_e^\ddagger}{RT} - \frac{\Delta F_\sigma^\ddagger}{f_0 \lambda g} \right\} 2 \sinh \frac{f}{2gf_0}. \quad (18)$$

If we write $\Delta F_e^\ddagger = \Delta H_e^\ddagger - T\Delta S_e^\ddagger$, we see that (18) can also be written as

$$\dot{S} = \frac{\lambda}{\lambda_1} \kappa \frac{kT}{h} \exp \left\{ \frac{\Delta S_{\text{app}}^\ddagger}{R} - \frac{\Delta H_e^\ddagger}{RT} \right\} 2 \sinh \frac{f}{2gf_0}, \quad (19)$$

where we have for $\Delta S_{\text{app}}^\ddagger$, the apparent activation entropy, the value

$$\Delta S_{\text{app}}^\ddagger = \Delta S_e^\ddagger + R \ln \kappa - \frac{\Delta F_f^\ddagger}{T_f} - \frac{R\Delta F_\sigma^\ddagger}{f_0 \lambda g}, \quad (20)$$

or, even more simply, we can define an effective activation entropy

$$\Delta S_{\text{eff}}^\ddagger = \Delta S_{\text{app}}^\ddagger + R \ln \frac{\lambda}{\lambda_1} \quad (21)$$

and write for the rate of shear

$$\dot{\epsilon} = \frac{kT}{h} \exp \left\{ \frac{\Delta S_{\text{eff}}^{\ddagger}}{R} - \frac{\Delta H_e^{\ddagger}}{RT} \right\} 2 \sinh \frac{f}{2gf_0} \quad (22)$$

The quantity $1/g = \lambda/x$ (see eqs. [11] and [22]) has the value 6.32, according to Tobolsky and Eyring's analysis³ of Trumpler's data for stress relaxation of steel.⁵ According to the theory, $1/g$ should approximate, as it does, the relative velocity of sound in the solid and the hypothetical vapor, provided that the distance, λ , which a patch jumps approximates a lattice distance. In this case, for steel, f_0 is the initial stress of the steel. Further, Tobolsky and Eyring found that ΔF^{\ddagger} decreases with increasing stress f_0 in accordance with the term $\Delta F_e^{\ddagger}/f_0\lambda g$ of equation (18). These authors also noted that $1/g$ is a constant for the creep of rubber at constant load. The form of the argument of the hyperbolic sine in equation (15) is of considerable interest. The interpretation of g has been given. In stress relaxation the local microstress, f_0 , has been identified as the initial macrostress. The independence of temperature of the argument of the hyperbolic sine has not previously been explained but has been widely observed.^{3, 6, 7} It has been found that equation (19), with $\Delta H_e^{\ddagger} = 0$, gives an excellent account of the plasticity of many metals at temperatures far below their melting points.⁷

* This work was supported in part by the Office of Naval Research.

¹ H. Eyring, S. Walter, and G. E. Kimball, *Quantum Chemistry* (New York: John Wiley & Sons, 1944), pp. 296-298.

² H. Eyring, *J. Chem. Phys.*, **4**, 283, 1936.

³ A. Tobolsky and H. Eyring, *J. Chem. Phys.*, **11**, 125, 1943.

⁴ Cf. Eyring, Walter, and Kimball, *op. cit.*, pp. 355-358.

⁵ W. E. Trumpler, Jr., *J. Appl. Phys.*, **12**, 248, 1941.

⁶ S. S. Kistler, *J. Appl. Phys.*, **11**, 769, 1940; W. Kauzmann, *Trans. Am. Inst. Mining Met. Engrs.*, **143**, 57, 1941; A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3, 1945; T. Ree and H. Eyring, *University of Utah Tech. Rept. (ONR)*, **28**, December 1, 1952; O. D. Sherby and J. E. Dorn, *Trans. Am. Inst. Mining Met. Engrs.*, (*J. Metals*), **194**, 959, 1952; *J. Metals (Trans.)*, **5**, 324, 1953.

⁷ J. W. Frederickson and H. Eyring, *Am. Inst. Mining Met. Engrs. Tech. Rept.*, **2423**, 1948.

INVESTIGATIONS ON LIGNIN AND LIGNIFICATION. XV. HETEROGENEITY OF NATIVE AND ENZYMATICALLY LIBERATED LIGNINS AS ESTABLISHED BY ELECTROPHORESIS AND PAPER CHROMATOGRAPHY

BY WALTER J. SCHUBERT* AND F. F. NORD

DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY,† FORDHAM UNIVERSITY, NEW YORK

Communicated by M. L. Wolfson, December 14, 1954

As it occurs in the natural state in wood, lignin is a complex polyphenolic compound, and it is generally assumed that it is formed through the polymerization of some fundamental unit, such as the phenylpropane moiety. This polymerization may occur through various possible linkages whose natures are as yet not established.¹