Application of Theory of Absolute Reaction Velocities to Creep of Metals*

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TO account for the influence of temperature on the rates of chemical reactions, S. Arrhenius introduced in 1889 the concept of activation energy, and he expressed the velocity constant, v, as a function of the temperature, in the form

$$v = A\epsilon^{-Q/RT}, \tag{1}$$

where

Q = activation energy per g-molecular mass,
R = gas constant per g-molecular mass, and
T = absolute temperature.

"The quantity Q represents the energy that the molecule in the initial state of the process must acquire before it can take part in the reaction, whether it be chemical or physical."[1]

The quantities v and A are evidently of the dimension of a frequency, ν, and H. Eyring has shown that the magnitude of this frequency may be calculated by application of the methods of statistical mechanics. "(This method) is based on the idea that a chemical reaction or other rate process is characterized by an initial configuration which passes over by continuous change of the coordinates into the final configuration. There is, however, always some intermediate configuration which is critical for the process, in the sense that if this system is attained there is a high probability that the reaction will continue to completion. This critical configuration is called the *activated complex* of the reaction."

This activated complex is regarded as being situated at the top of an energy barrier lying between the initial and final states.

On the assumption that the initial state is always in equilibrium with the activated state, it was shown by H. Eyring and his associates that the net rate at which the reaction occurs is given by a relation of the form

$$\nu = \frac{kT}{h}\cdot\epsilon^{-\Delta F/RT} \tag{2}$$

where k = Boltzmann constant = 1.3805×10^{-16} erg deg.$^{-1}$; h = Planck's constant = 6.624×10^{-27} erg sec.; and F = *free energy* of activation.

Since $\Delta F = \Delta Q - T\Delta\eta$, where η = entropy of activation and Q = energy of activation, Eq. (2) can also be written in the form,

$$\nu = \frac{kT}{h}\cdot\epsilon^{\Delta\eta/R}\cdot\epsilon^{-\Delta Q/RT}, \tag{3}$$

or

$$\log(\nu/T) = 10.319 + (\Delta\eta/4.577) - (\Delta Q/4.577T). \tag{4}$$

Equation (3) is the relation for the absolute velocity of any unimolecular reaction for which the activation energy is ΔQ.

Eyring and his associates have shown that this equation applies not only to chemical reactions but also to such purely physical phenomena as viscous flow and diffusion, since these may also be regarded as rate processes. More recently A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon[2] have applied Eyring's theory to the interpretation of measurements of stress decay in natural and synthetic rubbers made at constant elongation.

W. Kauzmann[3] showed that the relations deduced by Eyring for the case of viscous flow could also be applied to the creep of metals. In both cases the height of the potential energy barrier for flow in the direction of the applied shearing force or tensile stress is decreased by a quantity xRT calories per g-molecular or g-atomic mass in the direction of motion, and increased by the same amount in the reverse direction, where x varies linearly with the applied force.

* This paper is largely a summary of an article by S. Dushman, L. W. Dunbar, and H. Huthsteiner, J. App. Phys. **15**, 108 (1944).

[1] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 2. The reader is referred to this treatise for a comprehensive discussion of this subject. The passages quoted are taken from this book.

[2] A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, J. App. Phys. **15**, 380 (1944).

[3] W. Kauzmann, Metals Tech. **8** (June, 1941).

TABLE I. Creep constants.

Metal	ΔQ	$-\Delta\eta$	T	n
Constantan	40,360	41.4	750	50
Pure Al	14,100	70.6	673	1,400
Com'l Al	33,140	32.5	653	700
Al-Mg	9,540	78.8	653	700
Pt	42,100	61.5	1000	593
Ni-Mo	45,400	52.7	1000	38
Pb (1)	11,500	92		
Pb (2)	3,050	89		
Ag	12,700	53	500	100
Ag	29,900	75		
Cd	Single cryst.		300	27,000

As a consequence the net rate of flow in the direction of the force is given by a relation of the form

$$\nu=\frac{kT}{h}\epsilon^{\Delta\eta/R}\cdot\epsilon^{-\Delta Q/RT}\cdot(\epsilon^{x}-\epsilon^{-x}). \quad (5)$$

In the paper published by S. Dushman, L. W. Dunbar, and H. Huthsteiner,[4] it has been shown that for creep in metals, this equation leads to the relation for rate of creep, which has the form,

$$\nu=\frac{1}{l}\frac{dl}{dt}=\nu_0 T\epsilon^{-Q/RT}(\epsilon^{x}-\epsilon^{-x}), \quad (6)$$

[4] S. Dushman, L. W. Dunbar, and H. Huthsteiner, J. App. Phys. **15**, 108 (1944).

where

$$\log\nu_0=10.319+(\Delta\eta/4.577)$$

and

$$x=j\alpha S/(2RT).$$

In this relation, α denotes the volume in cm^3 per g-atom of the "unit of flow," S denotes the applied tensile stress in g cm^{-2}, and j denotes the conversion factor (2.39×10^{-8} cal. erg^{-1}). For $x\geqslant 1.60$ approximately, the second exponential term may be neglected, and Eq. (6) may then be written in the form,

$$\log(\nu/T)=\log\nu_0-(\Delta Q/4.577T)+\gamma S, \quad (7)$$

$$=\log(\nu_S/T)+\gamma S, \quad (8)$$

where

$$\alpha=3.830\times10^{8}\gamma T,$$

and

$$\Delta\eta=4.577(\log\nu_0-10.319).$$

The creep rates (values of ν) actually observed on 10- and 20-mil wires of a number of metals and alloys, for a series of temperatures, were in the range 10^{-6} to 10^{-5} sec.$^{-1}$. The values of ΔQ, $\Delta\eta$, α and $n=\alpha/V_0$ (where V_0=atomic volume) are given in Table I.