

The Reaction Rate Theory of Viscosity and Some of its Applications

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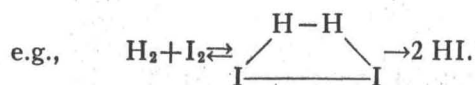


THIS article will be concerned with the fundamental theory of the flow of matter which results in permanent deformation, and its application to several types of viscous and plastic materials. The general features of the theory apply to flow

in all condensed phases, or more specifically to phases where viscous drag due to transfer of molecules between layers is negligibly small (i.e., gas type of viscous drag). This will include liquids of all sorts, glasses and resins, and crystals. About two years ago Eyring^{1, 2} published an ingenious treatment of viscosity, plasticity and diffusion wherein flow was considered as a unimolecular chemical reaction in which the elementary process is the passing of a molecule (or other unit of flow) from one equilibrium position to another over a potential energy barrier. Since this treatment is based on the modern theory of chemical reaction rates as developed by Tolman, Kassel, Rice, London, Polanyi, Wigner, LaMer, Rodebush, Eyring and others (and reviewed by Eyring³), a brief discussion of this theory will be given first.

The Theory of Chemical Reaction Rates

The most general treatment of reaction rates involves the concept of crossing a potential energy barrier by way of an activated complex



The rate constant, k_1 , for a reaction of any order in any phase is given by the equilibrium constant between the normal and activated states multiplied by the velocity at which the complexes cross the potential barrier and by the probability of their not returning. If the degree of freedom of the activated complex along which it approaches the potential barrier, crosses it and then flies to pieces, is taken as a translational one, we have:

$$\begin{aligned} k_1 &= \kappa K \frac{\bar{p}}{m} \\ &= \kappa K^* \frac{(2\pi mkT)^{\frac{1}{2}} \bar{p}}{h m} \\ &= \kappa \frac{F_a^*}{F_n} e^{-\Delta E_a/kT} \frac{(2\pi mkT)^{\frac{1}{2}}}{h} \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} \\ &= \kappa \frac{kT}{h} \frac{F_a^*}{F_n} e^{-\Delta E_a/kT}, \end{aligned} \quad (1)$$

$$\begin{aligned} \text{where } K &= \frac{\text{concentration of activated complex}}{\text{concentration of reactants}} \\ &= K^* \frac{(2\pi mkT)^{\frac{1}{2}}}{h}, \end{aligned}$$

Potential energy barriers seem destined to play an ever increasing role in modern physics. In the present paper their use in the theory of rates of chemical reactions is described. The general theory of such reactions has been extended recently so that it is applicable to problems involving viscosity, plasticity and diffusion not only in liquids but also in glasses, resins and crystals.—Editor