The temperature-dependence of the viscosity $\eta$ of a liquid can be described by means of an empirical equation suggested as early as 1921 by $\textit{Vogel}$: $\eta = A \exp(B/(T - T_0))$, which, besides the temperature $T$, contains three adjustable structure-dependent parameters $A$, $B$ and $T_0$. An equation of the same form is suited for describing the temperature dependence of the most probable relaxation time $\tau_m$ in polymers, and can be easily transformed into the so-called WLF-equation, because the empirical parameters $B$ and $T_0$ are simple functions of the WLF parameters. In many cases, the temperature-dependence of such quantities as mechanical or dielectric relaxation times, viscosities, diffusion coefficients etc., is regarded as a consequence of a thermal activation process ruled by a temperature-dependent Gibbs Free Energy of activation $\Delta G$. On the basis of this concept both parameters $B$ and $T_0$ can be related to the more fundamental high temperature limiting value of the activation energy $\Delta H$ and the parameter $T_m$ to the temperature at which $\Delta G$ becomes infinite. The parameter $A$ is normally taken to be temperature-independent; theoretically, however, it may just as well be temperature-dependent. Although it is difficult to decide from experimental evidence whether this case (accurate values over a large temperature range must be available), one should realize that analysis done by means of a temperature-independent pre-exponential factor gives a set of values for the parameters which differ greatly from those found when e.g. $A$ is set proportional to $T^{-1}$ or $T^{-2}$. Literature values for the viscosities of $n$-paraffins have been statistically analysed. It is concluded that $\eta$ in the $\textit{Vogel}$-equation had better be replaced by $\eta = A \exp(B/(T - T_0))$, where $Q$ is the density of the liquid. Values are given for the modified $\textit{Vogel}$, WLF and activation parameters of the paraffins and ethylene-co polymers, those for the latter being obtained from our own dielectric $\tau_m$ measurements. By analogy, $\tau_m$ then would have to be replaced by $\tau_m T^{2\gamma}$. However with our dielectric data, such a refinement would not give any great improvement.

I. Introduction

Thermally activated mechanical, electrical and diffusion processes in liquids and solids are often characterized by means of the energy parameter $\Delta H$, i.e. the heat of activation required for surmounting a free energy potential barrier. Often, values of $\Delta H$ are quoted which refer to the various relaxation processes observed in dynamic-mechanical, dielectric or viscosity measurements, in which case it is ignored that $\Delta H^+$, may be highly temperature-dependent, $\textit{Lawson}$ (1) and $\textit{Keyes}$ (2) investigated self-diffusion in inorganic solids; later, $\textit{Lawson}$ (3) studied the diffusion of impurities in amorphous polymers. These studies have shown that the ratio of entropy to enthalpy of activation $\Delta S^+ / \Delta H^+$ is approximately temperature-independent and equal to $4a$, where $a$ is the isobaric coefficient of the thermal volume expansion. $\textit{Eby}$ (4) confirmed this relation for the various relaxation processes observed in a number of polymers, which were mathematically analysed by means of the well-known equation:

$$\tau(T) = \tau_m(T) \exp(-\Delta H^+/RT) \exp(AS^+/R), \quad [1]$$

The correctness of $\textit{Eby}$'s finding depends on the way in which $\Delta H^+$ and $AS^+$ change with the temperature. It is our aim to propose an expression for the temperature-dependence of these quantities after giving an analysis of the literature viscosity data on normal paraffins. With this expression we shall then evaluate the activation quantities per mole of relaxing units on ethylene-vinylacetate (EVA) and ethylene-methacrylate (EMA) copolymers, using our dielectric data for these polymers. An analysis of the temperature-dependence of the Gibbs Free Energy of activation $\Delta G^+$ has already been given by $\textit{Ross Mac Donald}$ (5). Our treatment is therefore essentially the same as his, except that we used a simpler expression for $\Delta G^+(T)$, and furthermore made explicit allowance for the temperature-dependence of the pre-exponential term in eq. [1].

II. Empirical viscosity relations

The long history of equations describing the temperature-dependence of the viscosity of liquids and glasses dates back to as long ago as 1921 when $\textit{Vogel}$ (6) or $\textit{Fulcher}$ (7) and $\textit{Tamman}$ and $\textit{Hesse}$ (8) are reported to have advanced the equation

$$\eta = A \exp(B/(T - T_0)) \quad [2]$$

where $A$ and $B$ are temperature-independent constants and $T_0$ represents a transition temperature. Around 1940 (9) it became realized that the viscosity of polymers could be described by the product of a structure-sensitive factor $F$ and a temperature-sensitive friction factor per chain atom. The factor $F$ depends primarily on the degree of polymerization $Z$, so that

$$\eta = F(Z) \zeta(T). \quad [3]$$

Upon comparison of eqs. [3] and [2] it can be deduced that the temperature-dependence of $\zeta$ must have the form $\zeta(T) = \zeta_0 \exp(B/(T - T_0))$, where $\zeta_0$ is the in-
herent friction factor, which is presumed to be independent of $Z$ and $T$; and $A'/\zeta_0$ is only a function of $Z$. As to the $Z$-dependence of $A$ it appeared from isothermal viscosity measurements conducted in 1955, that $A$ was proportional to $Z^a$. It was found that at high molecular weights $a$ is constant and equal to 3.4, while below a critical molecular weight $a$ decreases with decreasing $Z$ from about 2.5 to 1.

However, theory (10) predicts that in isothermal measurements on long, entangled chains $A$ is proportional to $Z^{3.3}$, and in measurements on short chains proportional to $Z$. The discrepancy for low-molecular weight products was solved (11, 12), when it became realized that for short chains $\zeta$ is not only a function of temperature, but mainly owing to the molecular-weight dependence of the transition temperature $T_o$, also varies with $Z$.

Viscosity data relating to a constant value of $\zeta$ indeed show that in conformity with the theory $a = 1$ below a critical molecular weight. In 1951 Doolittle (13a) presented his free-volume viscosity equation; which is now mostly written in the form:

$$\eta = A' \exp(B'/f)$$

where $A'$ and $B'$ are structure-dependent, but temperature-independent constants, and $f$ is the free-volume fraction: $f = (V - V_0)/V_0$ where $V$ denotes the specific volume at temperature $T$ and $V_0$ the specific volume at temperature $T_0$. Doolittle first defined $V_0$ as the specific volume of the liquid extrapolated to temperature zero (13), but in a later article he used it as a third adjustable constant (13b). The physical significance of the temperature-dependence of the exponential term in the Vogel equation becomes clear if $f^{-1}$ is proportional to $(T - T_0)^{-1}$. This proportionality exists when the specific volumes $V_{1,s}$ of liquid and glass are linear functions of the temperature, but also, as pointed out by Matheson (14), in the more general case, when the densities $\rho_{1,s}$ are proportional to the temperature. We then have:

$$\rho_{1,s} = \rho_0 - \dot{\rho}_{1,s}(T - T_0),$$

where $\dot{\rho}_{1,s}$ represents the temperature derivative of the liquid and glass densities, so that the following relations between the Doolittle and Vogel parameters can be derived:

$$A' = A \exp[(B'q)/(\dot{\rho}_s - \dot{\rho}_g)]$$

$$B' = [(\dot{\rho}_l - \dot{\rho}_g)/\rho_0]B.$$  [5]

In 1955, Williams, Landel and Ferry (15) proposed the following empirical relation for the temperature-dependence of the frequency-shift factor $\log a_T$ of mechanical relaxations in amorphous polymers:

$$\log a_T = -c_1(T - T_o)/c_2 + T - T_s$$  [6]

where $c_1$ and $c_2$ are constants and $T_s$ is a reference temperature. This equation follows from the Vogel equation when $\log a_T$ is taken equal to $\log(\eta_T/\eta_{T_s})$; the WLF and Vogel parameters appear to be related as follows:

$$c_1 = B/2.303(T_s - T_o); c_2 = T_s - T_o.$$  [7]

Using the glass temperature for the reference temperature, it is found that $c_1$ is a nearly universal constant suggesting that the free volume fraction at $T = T_g$ is more or less constant. We must conclude therefore that for describing the temperature-dependence of the viscosity, the eq. [3], [4] or [6] do not offer a specific advantage over the Vogel equation. It must be remarked that the unsuitability of the Vogel equation for representing data covering a wide temperature range has been reported in studies on 1,3,5-tri-(p-naphthyl)-benzene (16) and glucose (17). Lamb and coworkers (18) from their work on supercooled liquids also arrived at the conclusion that they needed two sets of Vogel parameters for correlating their viscosity data over the entire temperature range investigated. However, the viscosity data by Napolitano, Macedo, and Hawkins (19) obtained on borontrioxide over the very large temperature range from 325-1400 °C, do satisfy the Vogel equation (see fig. 1). Nevertheless, to be quite safe, one had better compare the Vogel parameters for different polymers on the basis of viscosity data obtained in the same temperature range above $T_g$. So far, we have not made any suggestions as to how the Vogel equation might be improved; such improvements would necessarily involve the introduction of an extra adjustable parameter. From theoretical expressions to be given in section III it follows that the pre-exponential term may be temperature-dependent and proportional to the liquid density. This dependency can be accounted for empirically by introducing that value of $q$ for which a plot of $\ln(\eta T^q/\rho)$ versus $1/T - T_s$ shows the smallest standard deviation. In fig. 1, the $B_2O_3$ viscosity data are plotted for 3 arbitrarily chosen values of $q$; each line corre-