

Fig. 1. Effect of shear rate on intrinsic viscosity of polystyrene fractions. Solvent: benzene; temp.: 25°C; $C = 0.03-0.05$.

Bueche recognized that the coils are deformed in flow but was obliged to neglect the distinction between the natural and deformed states in his treatment. This omission has led Peterlin and Copic⁴ to speculate that the deformation and rotation had compensating effects and that if Bueche had not neglected this feature, he probably would not have found a dependence on velocity gradient.

The present writer has also treated this problem starting with essentially the same type of equations as those used by Rouse, written, however, for the general case where the perturbations resulting from all the components of the velocity gradient tensor are considered. The solution is initially determined in the polymer coil coordinate system but is transformed into laboratory coordinates since it is in terms of the latter that the steady state viscosity is usually measured. It is found that in the general case, there is a dependence of steady-state simple shear viscosity on velocity gradient. In the case where all the relaxation times have nearly the same value, the rotation and distortion compensate for each other; the effect predicted by Peterlin and Copic is then obtained and there is no variation of intrinsic viscosity with velocity gradient.

If the relaxation times given by Zimm⁵ for the non-free-draining case are used, the ratio of intrinsic viscosity at any velocity gradient K to the value obtained as $K \rightarrow 0$, is given as

$$\frac{[\eta]}{[\eta]_0} = 6.89 \times 10^2 \left\{ \sum_{k=1}^N \frac{\tau_k}{(1+K^2\tau_k^2)} + \left[\sum_{k=1}^N \frac{\tau_k^2 K}{(1+\tau_k^2 K^2)} \right]^2 / \sum_{k=1}^N \frac{\tau_k}{(1+\tau_k^2 K^2)} \right\}$$

when the relaxation times are $\tau_k = M\eta[\eta]_0 / 0.586RT\lambda_k'$ and the λ_k' values are given by Zimm *et al.*⁶ Equation (1) is shown plotted in Fig. 1 for two fractions of polystyrene dissolved in benzene at 25°C and compared with experimental values given by Sharman *et al.*⁷ The agreement is fairly good, considering that there is no adjustable parameter in the ratio $[\eta]/[\eta]_0$.

On the Infinite Multiplication Constant and the Age of the Uranium Minerals

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It has recently been pointed out by the author¹ that the values of the infinite multiplication constant, k_∞ , of the uranium minerals can be calculated according to the nuclear reactor theory²;

$$k_\infty = \epsilon p / f \eta \quad (1)$$

where, ϵ is the fast fission factor, p is the resonance escape probability, f is the thermal utilization factor, and η is the number of fast neutrons available per neutron absorbed by uranium.

The values of p , f , and k_∞ of a total of 20 samples of uranite, pitchblende, bröggerite, nivenite, and cleveite, of which complete chemical analyses are available in the literature,³⁻⁵ have been calculated and the results are summarized in Table I.

TABLE I. Calculated values of p , f , and k_∞ of the uraninites.

No.	Locality	p	f	k_∞	Pb/ (U+0.36 Th)
(1)	Placer de Guadalupe, Mexico	0.08	0.03	0.003	0.0046
(2)	Black Hawk, Colorado	0.30	0.90	0.36	0.009
(3)	Kirk Mine, Colorado	0.15	0.19	0.038	0.0115
(4)	Iizaka, Japan (cleveite)	0.10	0.006	0.001	0.0136
(5)	Hale's Quarry, Connecticut	0.12	0.30	0.048	0.040
(6)	Blanchville, Connecticut	0.13	0.91	0.16	0.052
(7)	Bonifrato, Brazil	0.20	0.21	0.06	0.067
(8)	Johanngeorgenstadt, Saxony	0.47	0.93	0.58	0.084
(9)	Shinkolobwe, Katanga	0.08	0.20	0.021	0.084
(10)	Morogoro, East Africa	(0.22) ^a	0.08	(0.023)	0.088
(11)	Nique-Nique, Brazil	0.40	0.21	0.11	0.102
(12)	Gustav's Mine, Norway (bröggerite)	0.16	0.09	0.018	0.123
(13)	Lac Pied des Monts, Quebec	(0.22) ^a	0.14	(0.040)	0.148
(14)	Wilberforce, Ontario	0.16	0.02	0.004	0.157
(15)	Baringer Hill, Texas (nivenite)	0.33	0.007	0.003	0.163
(16)	Arendal, Norway (cleveite)	(0.22) ^a	0.007	(0.002)	0.182
(17)	Great Bear Lake, Canada	0.37	0.08	0.041	0.202
(18)	Ingersoll Mine, South Dakota	0.09	0.08	0.010	0.226
(19)	Winnipeg River, Manitoba	(0.22) ^a	0.07	(0.020)	0.261
(20)	Sinyaya pala, Karelia, U.S.S.R.	0.29	0.024	0.009	0.30

^a The values of p cannot be calculated, since the water contents of the minerals are unknown. An assumed value of $p = 0.22$ (an average value of p of the 16 samples of minerals) has been used for the calculation of k_∞ .

In calculating the values of f , certain relative abundance patterns of the rare earths elements in the minerals had to be assumed, since the analyses of the individual rare earth elements were not available. The relative abundance pattern of the rare earths in igneous rocks was taken to be similar to that in the uranium minerals. Whenever the analytical results were expressed as the sum of two constituents, the weight ratio of the two was assumed to be 1 to 1.

Since the trace constituents of the minerals, of which quantitative determinations had not been made, may also absorb considerable fractions of the total neutrons available, the true values of f and k_∞ may be somewhat lower than the values given in Table I.

The resonance escape probability, p , depends upon the ratio of the moderator to uranium (fuel) in the system. H₂O is by far the best moderator available in the uranium minerals.

The infinite multiplication constant, k_∞ , is plotted against the Pb/(U+0.36 Th) ratio in Fig. 1.

It appears that the following rule holds; the greater the age of the mineral, the smaller the value of k_∞ , although the minerals with small values of k_∞ are not necessarily old.

A number of the rare earths elements have extremely large neutron absorption cross sections and the values of f are almost entirely dependent upon the rare earths contents of the minerals. The old minerals are always associated with considerable amounts of the rare earths, although the minerals with high rare earths

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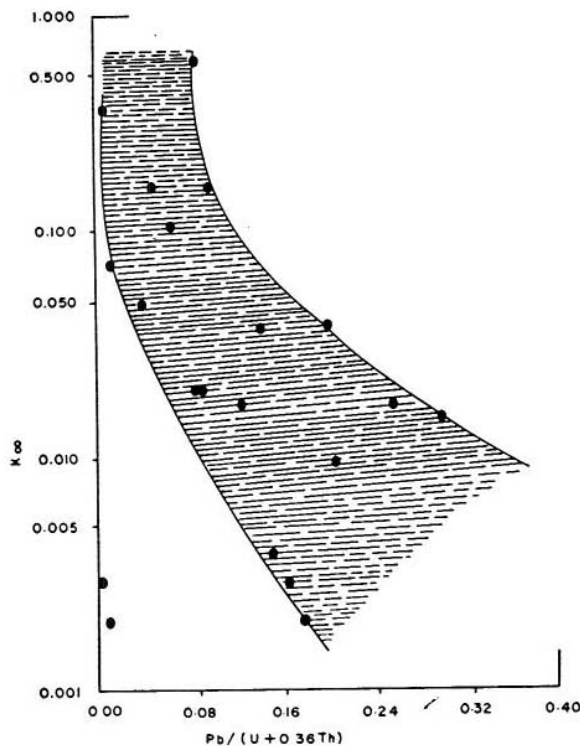


FIG. 1. Interrelationship between k_x and $Pb/(U+0.36Th)$ of the uranium minerals.

contents are not necessarily old. It is probably worthy of note that the interrelation becomes even more evident, if the $(Y,Er)_2O_3/U$ ratios are plotted against the $Pb/(U+0.36Th)$ ratios, while the relationship is not clear between the $(Ce,La)_2O_3/U$ ratios and the $Pb/(U+0.36Th)$ ratios.

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Nature of the Free Electron Approximation: The Simple Example of the H_2^+ Ion

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THE type of free electron model used in this laboratory may be viewed as depending on four special assumptions:

(I) Each one-electron wave function ψ may be approximated satisfactorily by a product $\psi = Ff$, where F depends on the coordinate along the molecular chain, i.e., the zig-zag line of the carbon atom skeleton, and f on the coordinates lying on a surface orthogonal to this line.

(II) The factor f is common to all states of the π electron, so that the i th state is $\psi_i = F_i f$.

(III) The functions F_i are eigenfunctions of the one-dimensional Schroedinger equation for an electron in a certain assumed

potential V , where V depends only on the coordinate along the molecular chain.

(IV) The energy of the i th state is $E_i = EF_i + E_f$. Here EF_i is the eigenvalue associated with F_i , and E_f is the average kinetic energy associated with the degrees of freedom perpendicular to the molecular chain.

The free electron model is useful because very simple assumed forms of V yield remarkably good excitation energies. In the simplest applications, V has been taken as constant along the molecular chain, rising to infinity at the ends.

In order to obtain detailed information about the effective potential V appropriate for π electrons, and to test assumptions (I) to (IV) critically in a simple case, we have applied the free electron approximation to the states of the H_2^+ ion with π -type symmetry. For the normalized wave function we take

$$\psi = F(x) f(\rho, \varphi) = F(x) \frac{4}{\beta^2 (6\pi)^{1/2}} \rho \cos \varphi e^{-\rho/\beta} \quad (1)$$

(x, ρ, φ are cylindrical coordinates about the bond axis, and β is an adjustable constant; $F(x)$ is symmetrical in x in the $2p\pi$ -bonding state, antisymmetrical in the $2p\pi$ -antibonding state). The function $F(x)$ and the value of β are found by minimizing $(\psi|H|\psi)$. The minimization was first carried out with respect to $F(x)$ and then, by repeating the treatment for various values of β , with respect to β . The problem of finding the function $F(x)$ which minimizes $(\psi|H|\psi)$ for a given value of β may be reduced to finding the solution of the Schroedinger equation

$$\frac{d^2 F}{dx^2} + \frac{8\pi^2 m}{h^2} [E_F - V(x)] F = 0. \quad (2)$$

Here $V(x) = (f|U|f)$ may be viewed as the average, over a plane normal to x , of the electrostatic interaction, $U(x, \rho)$, between the electron and the two protons, and

$$E_F = (\psi|H|\psi) - E_f, \quad (3)$$

where E_f is the average kinetic energy associated with coordinates ρ and φ and the function f .

We have solved Eq. (2) with the aid of an analog computer which will be described elsewhere. The lowest eigenvalue corresponds to the $2p\pi$ -bonding state, the next to the $2p\pi$ -antibonding state. The energies of these states are given in Table I. For comparison we also list the exact values as calculated by Teller, and the values obtained for a LCAO calculation using $2p$ functions and minimizing $(\psi|H|\psi)$ with respect to an effective nuclear charge.

Clearly the energy values are very satisfactory, indicating the validity of assumption (I) in this case. Similarly, the concept that excitation may be associated with the degree of freedom along the bond axis [assumption (II)] is justified by the identical values of β in both states. Assumptions (III) and (IV) are then justified in this case by Eqs. (2) and (3).

It may be shown that the effective potential $V(x)$ calculated here for a nuclear charge of unity and interatomic distance of 4.32 Å differs only by a scale factor from the $V(x)$ appropriate for a nuclear charge of 3.25 (Slater value for a $2p$ electron in carbon) and an interatomic separation of 1.33 Å (carbon-carbon double

TABLE I. Energy of $2p\pi$ states of H_2^+ .

	Calculated for interatomic distance of 4.32 Å; energy (including contribution of nuclear repulsion) in units of 10^{-11} erg.		
	electron gas model	exact	LCAO minimized with respect to effective nuclear charge
E_{bonding}	-0.56 ($\beta = 1.10\text{Å}$)	-0.58	-0.553
$E_{\text{antibonding}}$	-0.40 ($\beta = 1.10\text{Å}$)	-0.42	-0.416
$E_{\text{antibonding}} - E_{\text{bonding}}$	0.16	0.16	0.137