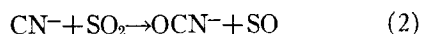
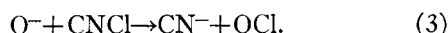


capture process for  $\text{SO}^-$  occurs at about 0.4 eV above that for  $\text{O}^-$  from  $\text{SO}_2$ . There is the possibility that the reaction



may occur. It is concluded that this reaction is not responsible for  $\text{OCN}^-$  formation because no ion current at  $m/e$  42 was found in the electron energy region where the resonance process for  $\text{CN}^-$  occurs. Furthermore Reaction (2) is endothermic by approximately 2 eV.

In preliminary experiments with only  $\text{CNCl}$  in the ion source the intensity of  $\text{CN}^-$  remained essentially constant as the ion residence time was increased. However, in the mixture of  $\text{SO}_2$  and  $\text{CNCl}$  a fourfold increase in the  $\text{CN}^-$  ion intensity was observed as the delay time was increased. The reaction occurred only at the resonance potential for  $\text{O}^-$  and is expressed by



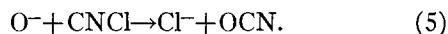
That  $\text{OCl}$  is the neutral product in the reaction is supported by the fact that Reaction (3) is exothermic by about 0.75 eV. If the neutral products are oxygen and chlorine atoms, the ion-molecule reaction is endothermic by 2.0 eV.

The formation of secondary ions was also investigated in the  $\text{N}_2\text{O}:\text{CNCl}$  system. The formation of  $\text{OCN}^-$  in this mixture may occur by either Reaction (1) or by



Using the values for the heats of formation of ions given below, Reactions (1) and (4) are each found to be exothermic by approximately 2.0 eV. In the experiments with  $\text{N}_2\text{O}:\text{CNCl}$ ,  $\text{OCN}^-$  was observed only at the resonance capture energy for  $\text{O}^-$ . As in the  $\text{SO}_2:\text{CNCl}$  mixture a prominent increase in the  $\text{CN}^-$  ion current must result from Reaction (3).

One reaction, which was exothermic by 5.9 eV, might have been expected to occur in either of these systems but was not observed:



The maximum intensity of  $\text{Cl}^-$  from  $\text{CNCl}$  occurred at an electron energy of 3 eV, so that the intensity of  $\text{Cl}^-$  was quite small in the electron energy range of  $\text{O}^-$  (about 2 and 4.2 eV maximum with  $\text{N}_2\text{O}$  and  $\text{SO}_2$ , respectively). The abundance of  $\text{Cl}^-$  remained small and constant within experimental error at the energy for the formation of  $\text{O}^-$  by dissociative resonance capture over the range of ion residence times studied, 0.25–2.0  $\mu\text{sec}$ . Thus if Reaction (5) occurred, it was to a very small extent. The large (5.9 eV) exothermicity of Reaction (5) is sufficient to cause the electron to be ejected from  $\text{Cl}^-$ , and hence the latter should not be formed.

Reaction-rate constants were determined by observing the variation in primary and secondary ion current

as a function of delay time at constant source pressure. The rate constant for the disappearance of  $\text{O}^-$  in  $\text{SO}_2:\text{CNCl}$  and  $\text{N}_2\text{O}:\text{CNCl}$  mixtures at 25  $\mu$  source pressure was found to be  $2.23 \times 10^{-9}$  cc/molecule sec. Since  $\text{O}^-$  is precursor to both  $\text{OCN}^-$  and  $\text{CN}^-$  it was necessary for comparison to determine  $K_1 + K_2$  after the method of Shannon and Harrison.<sup>4</sup> The sum of the rate constants was  $2.19 \times 10^{-9}$ , in excellent agreement with the rate constant for  $\text{O}^-$  disappearance.  $\text{OCN}^-$  was much less abundant than  $\text{CN}^-$ . The rate constant for its formation by Reaction (1) is approximately  $1.5 \times 10^{-10}$  cc/molecule·sec.

Heats of formation in kilocalories per mole employed are as follows:  $\text{CNCl}$ , 32.97;  $\text{OCl}$ , 24.34;  $\text{Cl}$ , 29.08;  $\text{O}$ , 59.553;  $\text{Cl}^-$ , -58.9;  $\text{O}^-$ , 24.29;  $\text{SO}_2$ , -70.944;  $\text{SO}$ , 1.496;  $\text{N}_2\text{O}$ , 19.61 (all from Ref. 5);  $\text{OCN}^-$ , -19 (Ref. 2);  $\text{CN}^-$ , 15 (Ref. 6);  $\text{OCN}$ , 17 (Ref. 7).

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## Relaxation Times and Normal Mode Frequencies

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In this Note, we shall show that in a uniformly damped harmonic solid, there is a simple relationship between normal mode frequencies and corresponding relaxation times. The solution of the relaxation-time distribution-function problem thereby reduces to obtaining the normal mode frequency spectrum of the array. This connection was previously postulated by one of us<sup>1</sup> to hold in one, two, and three dimensions, and is proven (within certain limitations) in this Note.

The thermal energy of a crystal or glass containing  $N$  particles is reflected in the small vibrations of these particles about their equilibrium positions in the lattice. The collective motion can be analyzed in terms of normal mode lattice vibrations, each mode having a characteristic frequency. The frequency distribution is of great importance in calculating the specific heat of

the solid. For the one-dimensional array, an exact frequency distribution has been derived in the classic work of Born and von Karman.<sup>2</sup> For an isotropic three-dimensional solid, the frequency distribution may only be approximated (Debye, Blackman, etc.<sup>2</sup>).

Consider a lattice in which the motion of each particle is uniformly damped. The equation of motion of the  $j$ th particle in the absence of external forces is

$$m\ddot{x}_j + f\dot{x}_j + \sum_{i=1}^N a_{ij}x_i = 0, \quad j=1, 2, \dots, N, \quad (1)$$

in the harmonic approximation, where  $x_j(t)$  is the displacement from equilibrium of the  $j$ th bead of mass  $m$  and friction factor  $f$ .<sup>3</sup> The quantities  $a_{ij}$  represent the interaction force constants between the  $i$ th and  $j$ th particles. In a one-dimensional lattice with nearest-neighbor interactions only, the sum reduces to

$$\alpha(2x_j - x_{j-1} - x_{j+1}), \quad (2)$$

where  $\alpha$  is the force constant between adjacent particles.

Equation (1) may be put in the form

$$m\ddot{q}_n + f\dot{q}_n + k_n q_n = 0, \quad n=1, 2, \dots, N, \quad (3)$$

by an appropriate transformation of coordinates. The  $q_n(t)$  are the normal coordinates of the motion.

Equation (3) is readily solved, and with the initial conditions that  $q_n(0) = \text{const}$  and  $\dot{q}_n(0) = 0$ ,

$$q_n(t) = [q_n(0)/(s_+^n - s_-^n)] [s_+^n \exp(-s_-^n t) - s_-^n \exp(-s_+^n t)], \quad (4)$$

where

$$s_{\pm}^n = (f/2m) [1 \pm (1 - \delta_n)^{1/2}], \quad (5)$$

with

$$\delta_n = 4mk_n/f^2.$$

Now in the strongly overdamped limit ( $\delta_n \rightarrow 0$ ) and for times longer than  $t = 4m/f(4 - \delta_n)$ , the first term of Eq. (4) dominates and the normal mode displacement decays in time according to

$$\langle q_n(0) q_n(t) \rangle \cong \langle q_n^2(0) \rangle \exp(-t/\tau_n), \quad (6)$$

where  $\tau_n = f/m\omega_n^2$ ,

$$\omega_n = (k_n/m)^{1/2}. \quad (7)$$

$\omega_n$  is the characteristic angular frequency of the undamped mode. Equation (7) for the relaxation time associated with the  $n$ th normal mode is fundamental in the present work and is seen to be independent of the dimensionality of the oscillator array. Such a relation was proposed to hold in all dimensions by one of us in 1962.<sup>1</sup> We see here that the postulate is true in the overdamped case and at long times. For very short times,  $q_n(t)$  decays as a Gaussian.

The Rouse-Bueche (RB) theory<sup>4,5</sup> of polymer viscoelasticity can be derived as a special case of the equations presented here. Since we are dealing with a linear lattice in this case, Eq. (2) must be substituted for the third term in Eq. (1). The constant  $\alpha$  for the RB theory is an entropic force constant (from rubber

elasticity theory) equal to  $3kT/\sigma^2$  where  $\sigma^2$  is the mean-square length of a Gaussian segment. The frequencies  $\omega_n$  are given by the Born-von Karman solution, namely

$$\omega_n^2 = (4\alpha/m) \sin^2(n\pi/2N), \quad n=1, 2, \dots, N. \quad (8)$$

(The normal-coordinate treatment of the linear lattice is given by Wannier.<sup>6</sup>) The relaxation times are related to the frequencies by our general solution, Eq. (7), and hence are

$$\tau_n = f/4\alpha \sin^2(n\pi/2N) \cong fN^2/\alpha\pi^2 n^2, \quad \text{for large } N, \quad (9)$$

In our general theory, presented in Eqs. (1)–(7), the force constants may be of any type (energetic or entropic) and Eq. (7) is valid for a lattice in one, two, or three dimensions. Equation (7) provides a unique connection between the relaxation-time spectrum and the frequency distribution as discussed in Ref. 1. An application of Eq. (7) to the theory of the viscoelastic response of polymeric—and simple organic—glasses is discussed in Ref. 7.

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### Retention of Additives in $Y_2O_3$ , $Gd_2O_3$ , $La_2O_3$ , and $\alpha-Al_2O_3$

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In the crystal growth of solid solutions, the various disparities between the additive and the host, such as ion size, valence, volatility, etc., characterize  $\rho$ , the retention coefficient. With  $Y_2O_3$  (mp 2450°C) as the host,  $\rho$  was obtained from the concentration ratio of crystal to powder. The crystals were grown by the Verneuil method with the trajectory distance,  $x_0$ , held constant. The concentrations were established by emission spectroscopy. For 10 4f(III) additives, Pr to Tm,  $\rho = 1.00 \pm 0.05$  in the concentration range 0.5–1.5 at.%. A more extensive range is shown in Fig. 1. If relative volatilities remained constant at the melting-point range of rare-earth sesquioxides, 2250°C  $\pm$  200°C, reciprocity would be expected. Indeed,  $\rho \approx 1$  is observed for Nd(III) and Eu(III) in host crystals  $Gd_2O_3$  (mp 2350°C) and  $La_2O_3$  (mp 2250°C).

If the bulk and surface of the powder differ in their