

Molecular Oscillation Frequency in Viscosity and Raman Effect

CALCULATIONS of viscosity on the basis of Andrade's theory have so far been made in the case of monatomic substances, whose frequencies of molecular oscillation are computed from Lindemann's expression. The viscosity η of such a substance at its melting-point is given by the formula:

$$= \frac{4}{3} \frac{M}{\sigma} \times 2.8 \times 10^{12} \sqrt{\frac{T_s}{MV^{2/3}}} \quad \dots (i)$$

More generally, for all substances including compounds we will assume that M denotes the molecular weight, V the molecular volume, T_s the melting-point and σ the mean distance between molecular centres. Calculating viscosity values for a number of organic substances from the formula (i), a fair agreement between the observed and the computed values is noticed.

TABLE I

Substance	η Calculated from (i)	η Observed*	Ratio $\frac{\eta \text{ Obs.}}{\eta \text{ Cal.}}$
Heptane ..	.002472	.00253	1.02
Pentane ..	.002223	.00256	1.15
Octane ..	.002648	.00244	0.92
Propyl Chloride ..	.002770	.00352	1.27
Propyl Bromide ..	.003574	.00388	1.08
Propyl Iodide ..	.004058	.00420	1.03
Carbon tetrachloride	.004811	.00654	1.35
Chloroform ..	.004278	.00465	1.08
Benzene ..	.003766	.00391	1.03
Ethyl Benzene ..	.002817	.00282	1.01
Ethyl Sulphide ..	.00275	.00279	1.01
Carbon Bisulphide	.003715	.00367	0.99
Propyl Acetate ..	.002895	.00304	1.05
Methyl Formate ..	.003387	.00384	1.13

* Macleod, *Proc. Phys. Soc.*, 1938, 53, 788.

The mean value of 1.08 for the ratio indicates the general applicability of Lindemann's

expression. Further the Lindemann frequency which is generally accepted to coincide with the Debye maximum frequency or the Reststrahlen frequency often gives rise to a Raman line in the scattered radiation from such monatomic substances as diamond, phosphorus, sulphur, etc. Some of the Raman lines observed close to the Rayleigh line by Gross and Vuks¹ as well as Sircar and Gupta² in some organic crystals seem to arise from the same source.

TABLE II

Substance	ν Calc. in cm.^{-1}	ν Obs. (Raman Spectra) in cm.^{-1}
Diamond ..	1302	1332
Calcium Fluoride ..	330.6	322
Sodium Chloride ..	195.9	235
<i>p</i> -Dibromobenzene ..	23.32	20.1
<i>p</i> -Dichlorobenzide ..	30.03	27.6
Naphthalene ..	36	42
Ammonium Chloride ..	171	160
Phosphorus ..	27.5	36
Sulphur ..	88	85
Mercurous Chloride ..	316	312
Aragonite ..	107.3	91

The existence of the Lindemann or the Debye maximum frequency in the scattered spectra favours the view that the Raman lines close to the Rayleigh line arise from lattice oscillations.

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¹ Gross and Vuks, *Nature*, 1935, 135, 998; *Journal de Phys. et le Radium*, 1936, 7, 113; and *Vul. s. C.R. de l'Acad. des Sc., U.S.S.R.*, 1936, 1, 72.

² Sircar and Gupta, *Ind. Jour. Phys.*, 1938, 12, 35-46; and 1936, 10, 473.