

LETTERS TO THE EDITOR

CALCULATION OF HIGH FREQUENCY DIELECTRIC CONSTANT OF ALKALI HALIDE CRYSTALS

THE high frequency dielectric constant (ϵ_{∞}) of alkali halide crystals can be expressed by Lorentz-Lorenz relation as

$$\frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} = \frac{4}{3} \pi N (\alpha_+ + \alpha_-) \quad (1)$$

where α_{\pm} are the polarisabilities of alkali and halogen ions, and N, the number of ion pairs per unit volume, is given by

$$N = \frac{1}{Kr^3} = \frac{1}{K(R_+ + R_-)^3} \quad (2)$$

where r is the interionic distance and can be written approximately as the sum of the ionic radii R_+ and R_- in alkali halide crystals. The value of K is 2 and 1.54 for NaCl and CsCl type structures respectively. From equations (1) and (2) we can deduce

$$\alpha_+ = \eta_+ R_+^3 \quad (3)$$

and

$$\alpha_- = \eta_- R_-^3 \quad (4)$$

with

$$\eta_+ = \frac{3K}{4\pi} \left(1 + \frac{R_-}{R_+} \right)^3 \left(\frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \right) \quad (5)$$

and

$$\eta_- = \frac{3K}{4\pi} \left(1 + \frac{R_+}{R_-} \right)^3 \left(\frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \right) \quad (6)$$

It has been shown by Jai Shanker *et al.*¹ that the values of η_+ or η_- for an ion is nearly constant in different crystals or in free state, i.e., vacuum. Therefore, we can determine the values of η_{\mp} from equations (3) and (4) using the free ion polarizability values of Pauling² and radii cited in Kittel³.

$\left(\frac{\alpha_-}{\alpha_+}\right)$ or $\left(\frac{\alpha_+}{\alpha_-}\right)$ in equation (5) or (6) can be eliminated from (3) and (4) and then the transformed forms of expressions (5) and (6) will only relate the high frequency dielectric constant of crystals, ionic radii and dimensionless constants. Using the ionic radii values of Fumi and Tosi⁴, and Bansigir⁵, we have calculated the high frequency dielectric constant of alkali halide crystals listed in Table I.

TABLE I
Values of the high frequency dielectric constant * of alkali halide crystals

	Li	Na	K	Rb	Cs
F	1.76	1.60	1.77	1.88	2.28
	1.93	1.74	1.85	1.93	2.16
Cl	2.75	2.14	2.09	2.13	2.84
	2.75	2.33	2.17	2.18	2.63
Br	3.17	2.33	2.18	2.22	2.98
	3.16	2.60	2.36	2.34	2.78
I	3.82	3.02	2.44	2.43	3.23
	3.80	3.01	2.65	2.58	3.02

* For each alkali halide the first row value gives the calculated high frequency dielectric constant and second row gives the experimental value of high frequency dielectric constant.

The results are in general agreement with the experimental values⁶ and the maximum disagreement can be considered nearly 10% which may be due to the approximate additivity rule implied in the derivation of equations (5) and (6) and can also be attributed to the difference between available radii data^{4,5}.

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THERMODYNAMIC PROPERTIES OF SOME MOLECULES OF XO_2Y_2 AND XO_2YZ TYPES

THE calculation of thermodynamic properties, viz., heat content $(H^\circ - E_0^\circ)/T$, free energy $-(F^\circ - E_0^\circ)/T$, entropy S° and heat capacity C_p° is one of the essential applications of the study of the vibrational spectra of polyatomic molecules. The necessary details of the calculations are given

by Colthup¹, Pitzer², Taylor and Glasstone³ and several others⁴⁻⁷.

The energy of a molecular system may be treated as the sum of the energies of the translational, rotational, vibrational, electronic and nuclear spin motions. The ground electronic state has been considered here and the nuclear spin energy has been neglected, its contribution being poor. A rigid rotor harmonic oscillator model with no interaction between vibrational and rotational energies is assumed.

On the basis of the above assumptions the thermodynamic properties were calculated for the temperature range 100° K to 1000° K for the ideal gaseous state at one atmosphere pressure in the case of sulphuric acid $\text{SO}_2(\text{OH})_2$ and selenic acid $\text{SeO}_2(\text{OH})_2$ of the XO_2Y_2 type molecule belonging to C_{2v} point group (Table I). The symmetry

TABLE I
 XO_2Y_2 type molecules

T (°K)	$H^{\circ} - E_0^{\circ*}$		$-(F^{\circ} - E_0^{\circ})^*$		$S^{\circ*}$	$C_p^{\circ*}$
	T	T	T	T		
$\text{SO}_2(\text{OH})_2$						
100	8.0665	48.2705	56.3369	8.6512		
200	9.2845	54.1773	63.4618	12.4749		
298.16	10.9049	58.1856	69.0904	15.7889		
300	10.9349	58.2528	69.1877	15.8427		
400	12.4915	61.6159	74.1074	18.3482		
500	13.8537	64.5534	78.4071	20.1559		
600	15.0177	67.1849	82.2026	21.4469		
700	16.0060	69.5763	85.5823	22.3756		
800	16.8468	71.7699	88.6167	23.0544		
900	17.5659	73.7968	91.3627	23.5602		
1000	18.1854	75.6804	93.8658	23.9444		
$\text{SeO}_2(\text{OH})_2$						
100	8.4068	50.0471	58.4539	10.0419		
200	10.5413	56.4993	67.0406	15.0052		
298.16	12.5924	61.1010	73.6934	18.3296		
300	12.6277	61.1786	73.8064	18.3805		
400	14.3568	65.0580	79.4248	20.6273		
500	15.7751	68.4208	84.1958	22.0844		
600	16.9118	71.4010	88.3128	23.0413		
700	17.8365	74.0798	91.9163	23.6889		
800	18.5980	76.5128	95.1108	24.1449		
900	19.2331	78.7411	97.9742	24.4687		
1000	19.7693	80.7961	100.5654	24.7111		

number is one. The principal moments of inertia as calculated in this work are:

$$\text{SO}_2(\text{OH})_2 \quad I_{xx} = 94.6253 \text{ a.m.u.A}^2, \quad I_{yy} = 98.1041 \text{ a.m.u.A}^2, \quad I_{zz} = 95.0132 \text{ a.m.u.A}^2.$$

$$\text{SeO}_2(\text{OH})_2 \quad I_{xx} = 114.5425 \text{ a.m.u.A}^2, \quad I_{yy} = 112.6643 \text{ a.m.u.A}^2, \quad I_{zz} = 116.2010 \text{ a.m.u.A}^2.$$

The observed wave numbers and necessary details were taken from the work of T. Birchall and R. J. Gillespie⁸ and of others⁹⁻¹¹.

Similar calculation was carried out using data of Reed and Lovejoy¹² in the case of sulphuryl bromide fluoride, (SO_2BrF) molecule of the C_s ,

point group under XO_2YZ type for temperature range 298.16° K to 1000° K (Table II).

TABLE II
 XO_2YZ type molecules

T (°K)	$H^{\circ} - E_0^{\circ*}$		$-(F^{\circ} - E_0^{\circ})^*$		$S^{\circ*}$	$C_p^{\circ*}$
	T	T	T	T		
SO_2BrF						
298.16	12.3761	63.0424	75.4188	17.7014		
400	13.9919	66.8990	80.8909	19.7645		
600	16.3939	73.0872	89.4812	22.2538		
800	18.3268	78.2309	96.5563	23.8430		
1000	19.2125	82.1363	101.3488	24.2609		

* = Cal. deg⁻¹ mole⁻¹.

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TETRAKIS SELENOUREA COBALT (II) PERCHLORATE

DIVALENT cobalt has a $3d^7$ non-bonding shell and usually forms tetra-, penta-, or hexa-co-ordinated complexes depending on the preparative conditions and polarisability of the ligand atoms. Tichane and Bennett¹ have shown that cobalt (II) has a weak class (b) character towards the donor atoms of