

Let us now assume that the vacuoles of radii  $R_{ni}$  be initially in a condition of stable equilibrium at a static pressure  $p_{ni}$ . Let the static pressure changes to some new value  $p_i$  and the new radii are  $R_i$ . We shall now investigate whether the vacuoles will be stable in this new position of equilibrium. The conditions for equilibrium of the vacuoles at the radii  $R_i$  under the new pressures  $p_i$  are

$$p_{ni} R_{ni}^S + R_i^S p_{vi} = R_i^S (p_i + 2\sigma/R_i),$$

$$i = 1, 2, 3, \dots, \quad (9)$$

$p_{ni}$  are the pressures inside the small vacuoles when  $R_i = R_{ni}$ ,  $p_{vi}$  are the vapour pressures and  $\sigma$  is the surface tension. The conditions give the radii at which the vacuoles will be in equilibrium. If the static pressures  $p_i$  are less than  $p_{vi}$ , the vacuoles will be in stable equilibrium only for radii for which  $R_i$  are less than the critical radii  $R_i^*$ , given by

$$R_i^* = \frac{(S-1) 2\sigma}{S | p_i - p_{vi} |} \quad (10)$$

Analogously, for the resultant vacuole we can write

$$R_n^* = \frac{(S-1) 2\sigma}{S | P_n - P_v |} \quad (11)$$

where  $P_n$  is the new pressure of the resultant vacuole and  $P_v$  is its vapour pressure. The critical radius of the vacuole itself is an unstable position. The resultant vacuole tends to vanish after coalescence and the cell then prepares to divide. In a collapsing vacuole, the changes of gas and vapour in it will ultimately be adiabatic ( $S=3\gamma$ ). During collapse, the cell fluid does work on the contents of the vacuole. Some of this work is transferred back to the cell fluid by heat conduction or by condensation of vapour at the interface. Small vacuoles are again generated in daughter cells and the cycle is repeated.

The theory is applicable to study the mechanics of etiology of decompression sickness where a formation of bubbles of  $N_2$  takes place<sup>4</sup> due to the fact that reduction of pressure has resulted in supersaturation of body fluids with  $N_2$ . In this case, the excess pressure is given by  $2\sigma/R$ .

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## MOLLWO-IVEY RELATION FOR KCl-KBr MIXED CRYSTALS

BRINDA SUBRAMANIAM\* AND K. G. BANSIGIR  
School of Studies in Physics, Jiwaji University  
Gwalior 474 001, India.

\*Present address: Department of Physics,  
Oklahoma State University, Stillwater,  
Oklahoma-74078, U.S.A.

THE  $F$ -band is a simple bell-shaped absorption band whose spectral position depends on the nature of the substance and temperature. For alkali halides having NaCl like structure it was found by Mollwo<sup>1</sup> that the position of the peak of the  $F$ -band at room temperature are fairly well related to its lattice constant and given by the expression

$$\epsilon \text{ (eV)} = 20.7 a^{-2}, \quad (1)$$

where  $a$  is the lattice constant of the alkali halides in Angstrom units and  $\epsilon$  the energy corresponding to peak of the absorption band in eV. A more accurate empirical relation was derived by Ivey<sup>2</sup> who found that

$$\epsilon = 17.6 a^{-1.84}. \quad (2)$$

To a good approximation, then the spectral location of the  $F$ -band at a given temperature is determined primarily by the lattice constant of alkali halide in question. This holds true not only for the pure alkali halides but also for solid solutions of these salts. Now several workers working in this field have given Mollwo-Ivey relation for different defect centres in alkali halides e.g. Radha Krishna and Kargupikkar<sup>3</sup> have given Mollwo-Ivey relation for  $U_1$ ,  $U_2$  and  $R_2$  bands; Hingsammer and Jodl<sup>4</sup> gave empirical relation for  $Z_1$  and  $Z_2$  centres in alkali halides doped with impurities.

Miessner and Pick<sup>5</sup> found that the  $F$ -band peak position in a series of KCl-KBr and KCl-RbCl solid solutions follow Mollwo's formula. Later Smakula *et al*<sup>6</sup> while studying the colour centres in mixed crystals of alkali halides pointed out that the ionic distance in mixed crystals changes linearly with composition but the spectral position of the  $F$ -band does not. It deviates towards lower energy reaching a maximum deviation of 0.03 eV for 1:1 composition. A group of Russian workers<sup>7,8</sup> also supported the views of Smakula *et al*<sup>6</sup>. Later Hovi and Passio<sup>9</sup> remarked that

mixed crystals show a small deviation from the Mollwo-Ivey line joining the two points corresponding to pure crystals of KCl and KBr.

In the midst of so many controversial views existing in this field regarding Mollwo-Ivey relation for mixed crystals we made an attempt to obtain this relation empirically. Single crystals of pure KCl, KBr and mixed crystals of KCl-KBr grown from melt were irradiated with a gamma dose of  $10^6$  R from a  $\text{Co}^{60}$  source at room temperature. The absorption spectra were recorded using Cary 14 spectrophotometer in the range of 300 nm to 700 nm. Such high doses ( $\sim 10^6$  R) were necessary for mixed crystals as it was difficult to colour these crystals. The spectra were recorded on a number of samples cleaved from different portions of the ingot to care of variation in composition within the ingot. Energy corresponding to *F*-band maxima for pure KCl, KBr and mixed crystals are compiled in table I.

TABLE I

Comparison of energies corresponding to absorption band maxima

Crystal	$\epsilon$ (eV) using eqn (3)	$\epsilon$ (eV) using eqn (5)	$\epsilon$ (eV) experimental
$\text{KCl}_{0.86}\text{Br}_{0.14}$	2.11	2.11	2.13
$\text{KCl}_{0.79}\text{Br}_{0.21}$	2.10	2.10	2.10
$\text{KCl}_{0.71}\text{Br}_{0.29}$	2.08	2.08	2.09
$\text{KCl}_{0.61}\text{Br}_{0.39}$	2.06	2.06	2.06
$\text{KCl}_{0.52}\text{Br}_{0.48}$	2.04	2.05	2.05
$\text{KCl}_{0.41}\text{Br}_{0.59}$	2.02	2.03	2.03
$\text{KCl}_{0.29}\text{Br}_{0.71}$	2.00	2.01	2.01
$\text{KCl}_{0.15}\text{Br}_{0.85}$	1.97	1.98	1.98

We considered the fact Mollwo-Ivey line joining the points corresponding to KCl and KBr do not include points corresponding to mixed crystals<sup>6-8</sup>. The mixed crystals show a small deviation from this line joining pure KCl and KBr<sup>9</sup>. Hence the points corresponding to pure crystals have not been considered and a graph is plotted between calculated values of  $\log_{10} a$  and observed values of  $\log_{10} \epsilon$ , as usual for KCl-KBr mixed crystals (figure 1). It is clear from figure 1 that  $\log_{10} a$  is linearly related to  $\log_{10} \epsilon$ . The slope of the straight line is -2.133 and its intercept on the Y-axis is 24.75. The result can be represented by the following equation

$$\epsilon = (24.75)a^{-2.133} \quad (3)$$

where  $\epsilon$  is expressed in eV and  $a$  in Angstrom units.

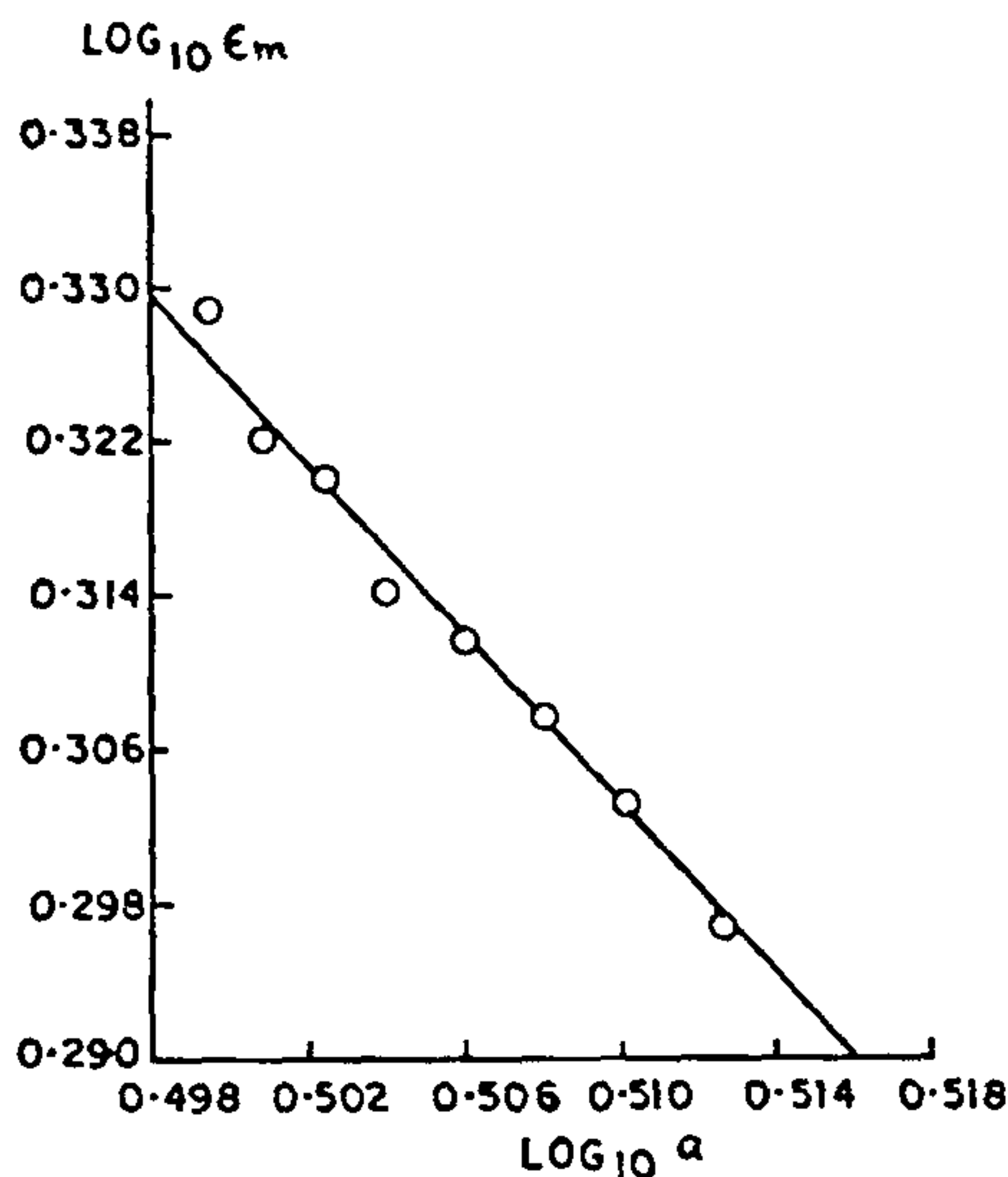


Figure 1. A plot of  $\log_{10} \epsilon$  vs  $\log_{10} a$  for all composition of KCl-KBr mixed crystals. X-axis represents  $\log_{10} a$ . Y-axis represents  $\log_{10} \epsilon$

The lattice constant for the mixed crystals has been calculated using a general relation proposed by Slagle and McKinstry<sup>10</sup>. It is well known that Mollwo-Ivey relation for alkali halides and hence for KCl and KBr is given by the expression (2). Assuming a linear interpolation we can express the energy corresponding to absorption band maxima for mixed crystals as

$$\epsilon_m = C_1 \epsilon_1 + C_2 \epsilon_2 \quad (4)$$

where  $\epsilon_1$  and  $\epsilon_2$  are the energies of *F*-band maxima for KCl and KBr respectively and  $C_1$  and  $C_2$  are the mole fraction of the two components in the mixed crystal. Expressing  $\epsilon_1$  and  $\epsilon_2$  in the form of Mollwo-Ivey relation we obtain

$$\epsilon_m = (17.6) a_{\text{KCl}}^{-1.84} \cdot C_1 + (17.6) a_{\text{KBr}}^{-1.84} \cdot C_2 \quad (5)$$

To test the validity of Mollwo-Ivey relation for KCl-KBr mixed crystals the energies calculated by using expression (3) and (5) are compared with experimentally observed values of  $\epsilon$ . These values of energy for the entire system are compiled in table I. A close agreement between different values show that Mollwo-Ivey relation holds good for solid solutions of alkali halides also. The Mollwo-Ivey line joining the two pure components do not include points corresponding to mixed crystals. The slope and intercepts



were also found to be different from that of pure crystals.

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## A STUDY OF SOME TOXIC CONSTITUENTS OF FIVE NEW VARIETIES OF PIGEON PEA (*CAJANUS CAJAN* (L) MILL SP.)

S. K. SHRIVASTAVA AND R. K. BAJPAI  
Department of Applied Chemistry, Government Engineering College, Jabalpur, 482 011, India.

LEGUMES are generally associated with cyanogenetic glycosides, tannins, trypsin inhibitors, phytohemagglutinins, goitrogens (in soybean and pea nuts), estrogens (in soybean), mimosene, a toxic amino acid (in *Leucaena glauca*); djenkolic acid (in *Pithecolobium lobatum*); and dihydroxyphenylalanine (in Indian variety of *Mucuna* seeds)<sup>1</sup>. In kidney bean<sup>2</sup> and in soybean, an antivitamin E factor has been reported. The toxic principles associated with pigeon pea are generally cyanogenetic glycosides<sup>3</sup>, and trypsin inhibitors<sup>4-6</sup>. Since the toxic principles of the pigeon pea varieties under study are not known, attempts have been made to study the cyanogenetic glycosides, tannins and phytohemagglutinins.

All the five varieties of pigeon pea (*Cajanus cajan* variety T-21, JA-9-19, JA-3, Gwl-3 and JA-15) were procured from Jawaharlal Nehru Krishi Vishwa Vidyalaya, Jabalpur, India.

Cyanide and tannin content of the seeds were determined by the method of AOAC<sup>7,8</sup> whereas the method of Liener<sup>9</sup> was employed for phytohemagglutinins. The effect of phytohemagglutinins was studied in the blood of rabbit, goat and sheep.

The cyanide content of the seeds varied from 0.45 to 0.70 mg HCN/100 g seed, which was found to be in general agreement with most of the legumes<sup>3,10</sup>. Var. JA-3 had the highest cyanide content (0.70 mg HCN/100 g seed) whereas Var. JA-15 had the lowest (0.45 mg HCN/100 g seed) (table 1).

TABLE 1

### Toxic constituents in Pigeon pea

Variety	Cyanide content mg HCN/100 g Seeds	Tannin content g/100 g Seeds
T-21	0.56	—
JA-9-19	0.54	0.67
JA-3	0.70	0.67
Gwl-3	0.54	1.26
JA-15	0.45	0.33

No hemagglutinin was found in these samples. The values are average of three independent determinations.

The tannin content of the seeds ranged from 0.33 to 1.26%, falling in line with other legumes<sup>10</sup>. It was highest in Var. Gwl-3 (1.26%), and lowest in Var. JA-15 (0.33%) (table 1).

Honovar *et al.*<sup>4</sup> failed to obtain agglutinating effect of pigeon pea seeds on the blood of rat. In the present investigation also agglutinating effect was studied on the blood of rabbit, goat and sheep but no positive effects were observed.

From the perusal of the data it appears that the percentage of different toxic principles in the five varieties of pigeon pea under study was comparatively<sup>11,12</sup> small (fatal dose recorded for hydrocyanic acid<sup>11</sup> is 50 mg/kg and fatal dose for tannic acid<sup>12</sup> is 6000 mg/kg).

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