

Spectrochemical Investigation of the Stability of Calcium Monohalogenides

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A new spectrochemical method of the relative stability evaluation of monohalogenides of the II. major subgroup of periodic system was developed using the relative intensities of the CaF, CaCl, CaBr, and CaI band edges. The investigation was carried out with an intermittent alternating current arc of 25 c/s which provides the plasma of discharge with a continuous supply of individual halogenides. On the basis of the results obtained from the band spectra of corresponding monohalogenides it may be concluded that a certain equilibrium becomes established with respect to individual monohalogenides in plasma which can be expressed by the relative intensities of individual band edges. These intensities exhibit a decreasing tendency in the sequence $\text{CaF} \rightarrow \text{CaCl} \rightarrow \text{CaBr} \rightarrow \text{CaI}$. On the basis of this phenomenon a decreasing stability in this series of monohalogenides may be assumed.

Halogenides of alkaline earth metals emit in electric discharge the band spectra of the type MX where M and X denote the metal and halogen respectively. That means that monohalogenides are involved in this process. This phenomenon was experimentally proved by *Walters* and *Barrat* [1]. *Olmsted* [2] studied carefully these spectra excited in flame. *Wieland* [3] paid attention to the composition of vapour and gases at high temperatures and pointed out that the halogenides of the II. major subgroup of periodic system partially decompose into elements but mainly into radicals $\text{MX}_2 \rightleftharpoons \text{MX} + \frac{1}{2}\text{X}_2$. Similarly *McTaggart* [4] described the dissociation of vapour of the halogenides of alkaline earth metals in electric discharge and pointed out that the halogenides of bivalent alkaline earth metals dissociated into monovalent molecules of halogenides — monohalogenides — and halogen ion or atom according to the equation $\text{MX}_2 \rightleftharpoons \text{MX} + \text{X}$ (or X^-). Since this investigation is concerned with the interaction of individual calcium monohalogenides in plasma which is examined by means of the relevant band spectra, it is to be noted that the preceding study has shown [5] that the monohalogenides of alkaline earth metals are not formed in the crater but in the plasma of electric arc by recombination of the particles originated from individual halogenides because of their dissociation:



This result explaining the formation of monohalogenides in plasma enables us to investigate the interaction of the components on the basis of their band spectra and thus to examine the stability of calcium monohalogenides.

Experimental

To investigate the stability of calcium monohalogenides, *i.e.* CaF, CaCl, CaBr, and CaI, it was necessary to work up the conditions under which a uniform evaporation of

Table 1

Optical and exciting conditions suitable for a resolved spectrum

Spectrograph	glass three-prism ISP-51
Lighting system	three-lens with intermediate imaging
Height of the intermediate stop	0.8 mm
Electrodes gap	4 mm
Slit width	0.004 mm
Carrier electrode	SU-308
Counter-electrode	SU-202
Exciting source	BIG 300
Effective voltage	100 V
Polarity	±
Phase	$\lambda/4$
Photographic material	ORWO panchromatic, NP-22
Exposure	10 s \times 12
Development	Rodinal R 09; dilution 1 : 25; 3'45" at 18°C

Table 2

Optical and exciting conditions differing from those quoted in Table 1

Height of the intermediate stop	5 mm
Photographic material	ORWO Rot Extrahart WP-3
Exposure	30 s
Development	4' at 18°C

Table 3

Wave lengths (nm) of the CaF, CaCl, CaBr, and CaI band edges used for the measurements of density

CaF	529.28	605.98
CaCl	593.54	621.14
CaBr	627.77	
CaI	638.88	641.29

Table 4

Relative intensity values of the CaCl, CaBr, and CaI band edges related to the unit intensity value of the band edge with the wave length of 605.98 nm

I [nm]	I_{CaF} 529.28	I_{CaF} 605.98	I_{CaCl} 593.54	I_{CaCl} 621.14	I_{CaBr} 627.77	I_{CaI} 638.88	I_{CaI} 641.29
CaF ₂ -CaCl ₂	0.084	1.00	0.435	0.685	—	—	—
CaF ₂ -CaBr ₂	0.10	1.00	—	—	0.372	—	—
CaF ₂ -CaI ₂	0.10	1.00	—	—	—	0.081	0.073

Table 5

Relative intensity values of the CaF, CaBr, and CaI band edges related to the unit intensity of the CaCl band edge with the wave length of 593.54 nm

I [nm]	I_{CaF} 529.28	I_{CaF} 605.98	I_{CaCl} 593.54	I_{CaCl} 621.14	I_{CaBr} 627.77	I_{CaI} 638.88	I_{CaI} 641.29
CaCl ₂ —CaF ₂	0.214	2.55	1.00	1.71	—	—	—
CaCl ₂ —CaBr ₂	—	—	1.00	2.22	1.34	—	—
CaCl ₂ —CaI ₂	—	—	1.00	1.71	—	0.254	0.225

Table 6

Relative intensity values of the CaF, CaCl, and CaI band edges related to the unit intensity of the CaBr band edge with the wave length of 627.77 nm

I [nm]	I_{CaF} 529.28	I_{CaF} 605.98	I_{CaCl} 593.54	I_{CaCl} 621.14	I_{CaBr} 627.77	I_{CaI} 638.88	I_{CaI} 641.29
CaBr ₂ —CaF ₂	0.392	2.86	—	—	1.00	—	—
CaBr ₂ —CaCl ₂	—	—	0.74	1.61	1.00	—	—
CaBr ₂ —CaI ₂	—	—	—	—	1.00	—	0.215

Table 7

Relative intensity values of the CaF, CaCl, and CaBr band edges related to the unit intensity of the CaI band edge with the wave length of 641.29 nm

I [nm]	I_{CaF} 529.28	I_{CaF} 605.98	I_{CaCl} 593.54	I_{CaCl} 621.14	I_{CaBr} 627.77	I_{CaI} 638.88	I_{CaI} 641.29
CaI ₂ —CaF ₂	1.46	14.6	—	—	—	1.11	1.00
CaI ₂ —CaCl ₂	—	—	4.48	7.68	—	1.11	1.00
CaI ₂ —CaBr ₂	—	—	—	—	4.87	—	1.00

the corresponding halogenides took place. *Pliško* [6] states that the importance of a uniform evaporation of particular components consists in the fact that practically an equal temperature of discharge is kept during the whole exposure time as well as the relative content of the particles investigated remains constant. Besides, the relative occurrence of the components in plasma may be considered proportional to the composition of sample during the whole exposure time. That is of fundamental importance especially to the method of partial evaporation of sample which has been used in this study. The resolved spectrum was taken under the conditions given in Table 1.

To investigate the stability of monohalogenides CaF, CaCl, CaBr, and CaI, present in molar ratio 1 : 1 without any addition of buffer, the following mixtures were prepared: CaF₂—CaCl₂, CaF₂—CaBr₂, CaF₂—CaI₂, CaCl₂—CaBr₂, CaCl₂—CaI₂, and CaBr₂—CaI₂.

There were some difficulties in preparing and photographing the samples because calcium chloride, bromide, and iodide are rather hygroscopic substances which begin

to moisten immediately after drying. After weighing and homogenization all samples were kept in a desiccator. To obtain approximately equal measurable values of the density of appurtenant band edges, each sample was always shot immediately after filling the electrode crater with it. The relevant conditions are given in Table 2 where only those parameters are quoted which differ from the ones listed in Table 1.

All spectra were taken 6 times. The measured values of the band edges of individual monohalogenides are presented in Table 3. The values of density found were transformed in the corresponding intensity values for each wave length of band edge using the characteristic density curves. For evaluation the intensity of a certain band edge was always considered to have a unit value with respect to which the intensities of other band edges in the spectrum were calculated. Thus the relative intensity values were obtained. The values listed in Tables 4–7 are mean values obtained from six measurements.

In the case of the pair CaF_2 – CaI_2 the CaF band edge having the wave length of 605.98 nm exhibited a very high density value which could not be read on photometer. In this case the intensity of the CaF band edge with the wave length of 529.28 nm was chosen as a unit value. As obvious from Tables 4–6, the intensity of the band edge with the wave length of 605.98 nm is about tenfold value of that with the wave length of 529.28 nm.

In the case of the pair CaBr_2 – CaI_2 the intensity of the CaI band edge with the wave length of 638.88 nm is not given because this band partially coincides with the CaBr band.

Results and Discussion

By the method of the relation curves related to the pair CaF_2 – CaCl_2 in molar ratio 1 : 1 a uniform evaporation in an intermittent alternating current arc of 25 c/s was achieved.

On the basis of the results thus obtained it may be concluded that an equilibrium is established with respect to individual monohalogenides in plasma. This equilibrium can be expressed by the relative intensity edges of the particular band spectra corresponding to CaF , CaCl , CaBr , and CaI . The values of the relative intensities of band edges given in Tables 4–7 have a falling tendency in the sequence $\text{CaF} \rightarrow \text{CaCl} \rightarrow \text{CaBr} \rightarrow \text{CaI}$. On the basis of this fact, a decreasing stability of the above monohalogenides in the sequence from CaF to CaI may be inferred.

The results obtained can be confronted with the known data on monohalogenides or halogenides [7, 8]. It is possible to compare the obtained results indicating the stability of individual calcium monohalogenides with the values of dissociation energies of CaF , CaCl , CaBr , and CaI which have been obtained by spectral methods [7]. The mentioned values of dissociation energies are:

Monohalogenide	CaF	CaCl	CaBr	CaI
Dissociation energy (eV)	3.15	2.76	2.7	2.5

Further it is possible to compare the obtained values of the relative intensities of individual calcium monohalogenides with the values of the heats of formation of the corresponding calcium dihalogenides in solid state [8]. The following values of these heats of formation have been quoted:

Halogenide	CaF_2	CaCl_2	CaBr_2	CaI_2
Heat of formation (kcal mol^{-1})	290.2 ± 5	190.4 ± 0.5	160.7 ± 2	128.5 ± 2.5

This method of the stability evaluation of compounds by means of band spectra enables us to appreciate the stability only relatively, *i.e.* we may make up a sequence with increasing or decreasing stability of individual compounds, but it is impossible to determine any absolute values characterizing the stability of a compound.

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