Fig. 2 — Plot of w^2 versus t at different temperatures for reaction between copper (plates) and bromine (vapour)

The average maximum thickness of the product film calculated from mass, theoretical density of the product γ-CuBr and the dimensions of the metal plate comes out to be 0·0026 cm. The reaction is a diffusion-controlled process. The product film which is coherent and protective controls the diffusion process.

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IR Spectrum of Benzoic Acid-Naphthalene Eutectic

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In naphthalene-benzoic acid system, certain C-H in-plane and out-of-plane frequencies of naphthalene and also C≡C bond stretching frequency of aromatic ring in benzoic acid are restricted, when the eutectic is formed. There, thus appears to be a definite orientation of naphthalene and benzoic acid with respect to each other in the eutectic mixture.

RASTOGI and Bassi[1] have made a comprehensive study of the growth characteristics and thermochemistry of eutectics formed between organic compounds. The growth kinetics and structure of the liquid eutectics have also been studied[2]. Savchenko[3] considers a eutectic to be formed by some sort of loose molecular or atomic interaction which does not involve the formation of a chemical compound, i.e. the formation of a eutectic leads to some merging of electron energy levels, but this is not accompanied by the formation of inter-atomic electrostatic bonds. Investigations have revealed that the mechanism of eutectic crystallization is quite complex. X-ray examination shows that a binary eutectic is a mixture of two kinds of crystals, favourably oriented with respect to each other[4]. Many eutectic composites have been reported by Hogan[5] to show a unique crystallographic orientations relationship both between constituent phases and their mating planes. After nucleation, many eutectics grow more or less perpendicular to the solidification front. Perfect lamellar grains have been found in lamellar Sn-Cd eutectic by Gruzleski and Winegard[6]. But in a number of systems, the eutectic grains do not exhibit a fixed crystal orientation with respect to external lines of reference[7]. IR reflectivity measurements of LiF-NaF lamellar eutectic by Proux and Racek[8] revealed that the difference in peaks may be due to interfacial phonones.

In view of these conflicting ideas, it was thought necessary to have some information regarding the character of eutectic from IR spectroscopy.

Naphthalene (USSR) was purified by sublimation (m.p. 80·3°) and benzoic acid (m.p. 121·2°, BDH, Analar) was used as such. Accurately weighed naphthalene and benzoic acid were taken in a tube, which was then sealed to avoid evaporation. The material in the tube was melted and then suddenly chilled in ice cold water 4-5 times. Tube was broken and the solid mixture thus formed was taken in agate crucible and powdered.

The phase diagram of naphthalene-benzoic acid system was determined by thaw melt method. Eutectic was found to be formed at 0·6670 molefraction of naphthalene with its melting point at 69·10° (ref. 9).

IR spectra (KBr) of the composite cannot be exactly superimposed on the spectra of constituent materials, naphthalene and benzoic acid. In the region 770 to 1030 cm^{-1}, a general decrease in intensities of the bands of eutectic in comparison with the parent compounds has been observed, e.g. the bands at 770 (s), 955 (m) and 1005 (m) cm^{-1} were reduced in intensity and appeared at 775 (m), 950 (sh) and 1005 (sh) cm^{-1} in the eutectic. Similarly bands at 800 (m) and 925 (m) cm^{-1} of benzoic acid appeared at 800 (sh) and 930 (m) cm^{-1} in the eutectic. Moreover, 978 (w) cm^{-1} band of naphthalene, which is due to out-of-plane homocyclic C—H deformation[10] was altogether missing in the eutectic. In-plane bending of C-H bond band 1020 (m) cm^{-1} of benzoic acid was diminished in intensity and shifted to 1030 (w) cm^{-1} in the eutectic.

In-plane bending bands 1237 (w) and 1265 (m) cm^{-1}, which are due to homocyclic C-H bond in naphthalene, were totally missing from the spectrum

of the eutectic. Further, out of 770 (s), 840 (w), 955 (m), 978 (w), 1005 (m), 1120 (m), 1140 (w), 1205 (w), 1237 (w) and 1265 (m) cm^{-1} bands of naphthalene, which are due to in-plane and out-of-plane bending of the C—H bond, all frequencies except 978 (m), 1237 (w) and 1265 (m) cm^{-1} appeared in the spectra of the eutectic. Moreover, it has been observed that bands of the same intensity as those of 978 (w), 1237 (w), and 1265 (m) cm^{-1} and sometimes even weaker bands did not disappear in the spectrum of the eutectic mixture. This suggests that absence of these bands in the eutectic is definitely due to some interaction at the molecular level. As only three frequencies of naphthalene, out of a number of them, are not reproduced in the spectra of eutectic, therefore, it can be concluded that the mating planes[11] of the constituent materials in the eutectic are such that these frequencies are hindered.

The band at 1450 (m) cm^{-1} in benzoic acid, is due to aromatic ring C=C bond stretching[12], was absent in the spectrum of the eutectic. Again, out of 1450 (m), 1470 (sh), 1500 (w), 1580 (w) and 1600 (w) cm^{-1} aromatic ring C=C stretching frequencies of benzoic acid, only the band at 1450 (m) cm^{-1} was missing in the spectrum of the eutectic, showing thereby that it is due to a specific positioning of benzoic acid in the eutectic. Band 1820 (w) cm^{-1} of benzoic acid, which is due to overtones and combinations, is missing in the eutectic and it will not have much significance[12]. Dimer character of benzoic acid in the eutectic, as revealed by IR spectrum, remains undisturbed.

It is evident that mating planes of parent compounds in the eutectic are such that three in-plane and out-of-plane C—H bending deformations of naphthalene and one aromatic ring C=C bond stretching frequency of benzoic acid are restricted. Therefore, it can be concluded that eutectic is a mixture having some specific orientation of the mating planes of constituent materials. This orientation appears to be even on the molecular level.

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12-Heteropoly Molybdotellurate

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A new 12-heteropoly molybdotellurate, $(NH_4)_2[TeMo_{12}O_{40}].15H_2O$, has been prepared and characterized on the basis of analytical and X-ray diffraction data. The X-ray data show that the system is orthorhombic with D_{2h}^2 space group.

THE preparation of 1:3, 1:4 and 1:6 heteropoly salts of molybdenum with tellurium has been reported in literature[1-4]. Preparation and characterization of a new 1:12 molybdotellurate is being reported here.

Aqueous solutions of telluric acid and ammonium molybdate, slightly acidified with acetic acid, were mixed in 1:12 molar ratio and refluxed for 2 hr. Excess liquor ammonia was added and the contents refluxed again for 4 hr. The solution was evaporated and allowed to crystallize *in vacuo* when small needle shaped yellowish crystals were obtained. These were recrystallized thrice from hot water. Analysis of the compound was carried out by chemical and colorimetric methods {Found: Te, 5·69; Mo, 51·80. Required for $(NH_4)_2[TeMo_{12}O_{40}].15H_2O$: Te, 5·73; Mo, 51·76%}. The analytical data were confirmed by estimation of N and H contents also. From the analytical data, the molecular formula of the compound as per Keggin's view[5] comes out to be $(NH_4)_2[TeMo_{12}O_{40}]15H_2O$. The compound can be designated as 12-heteropoly molybdotellurate.

The compound was studied by X-ray crystallographic method. The unit cell dimensions were determined using rotation and Weissenberg X-ray diffraction photographs. The crystal data obtained are as follows: $a = 10·66$ Å, $b = 25·12$ Å, $c = 9·29$ Å and $\alpha = \beta = \gamma = 90°$, hence the system is orthorhombic. The volume, V, per unit cell was calculated to be 2487·887 Å^3. The space group is established as D_{2h}^2-Pnnn, from the following systematic presence of reflections: hkl = no condition; $0kl = k+l = 2n$; $h0l = l+h = 2n$; $hk0 = h+k = 2n$; $h00 = (h = 2n)$; $0k0 = (k = 2n)$; $00l = (l = 2n)$ and $hkl = h+k+l = 2n$.

The number of molecules in the unit cell (z), is found to be 2. The observed density, measured by flotation method, was found to be $\rho_{obs} = 2·92$ g ml^{-1} against the calculated density, $\rho_{calc} = 2·97$ g ml^{-1} for the molecular weight 2225·61 of the compound $(NH_4)_2[TeMo_{12}O_{40}]15H_2O$.

The probable structure of the reported heteropoly salt may be similar to that suggested by Keggin[6] for the 12-heteropoly anion $[X^{n+}MO_{12}O_{40}]^{(8-n)-}$.

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