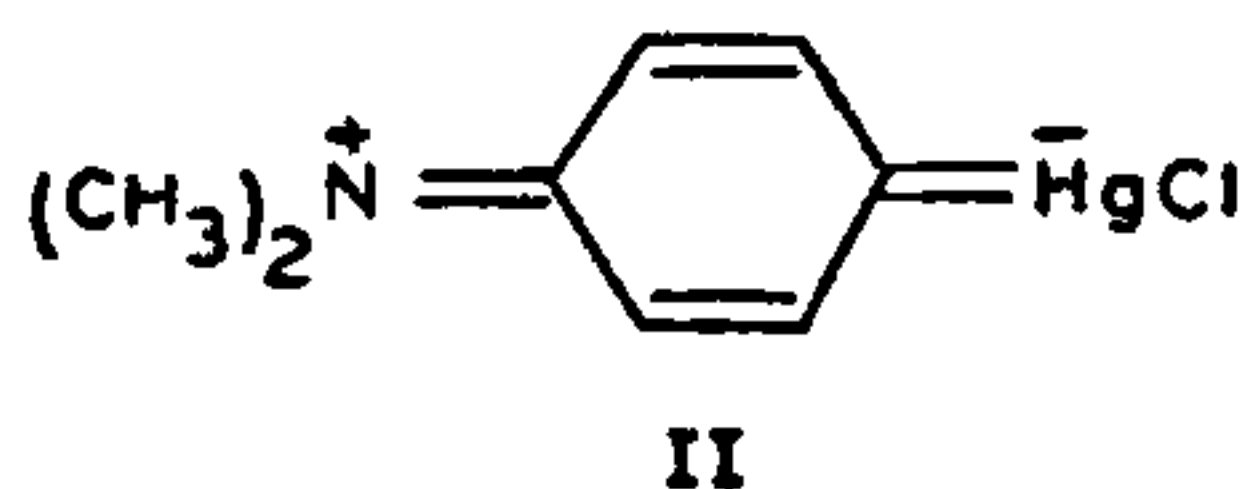


180°. In view of the fact that the observed dipole moment can vary by ± 0.02 D owing to experimental errors, the moment angles or bond angles computed from dipole moments are approximate and should only serve as useful guides in understanding the structure of molecules. Hence it may be concluded that the mercury valence angle in arylmercuric chlorides is very nearly 180°. This conclusion is also in accordance with the view that the two σ -bonds of mercury, resulting from 6s, 6p hybridized orbitals, should be linear.

The observed dipole moments 5.07 D and 4.94 D for the compounds 9 and 10 of table 1 are higher than the sums (4.92 D and 4.74 D respectively) of the group moments (dipole moments: $C_6H_5N(C_2H_5)_2$, 1.81 D⁹; $C_6H_5N(CH_3)_2$, 1.63 D¹⁰; C_6H_5HgCl , 3.11 D). The observed moment cannot be higher than the sum of the group moments without the existence of conjugative interaction of the *para* substituents. For example, the high moment of *p*-dimethylaminophenylmercuric chloride should be due to structure II making some contribution to its ground state.



This structure involves the utilization of one of its vacant 6p orbitals by mercury. Mercury can thus act as an electron acceptor and show a valence of 3.

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INTENSITY VARIATION OF X-RAY REFLECTIONS IN SINTERED MATERIALS

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SINTERED materials, with desirable mechanical, electrical and magnetic properties, are gradually replacing unsintered materials. Sintering is an agglomeration or consolidation of loosely packed or pressed fine powder particles by heat treatment below the melting temperature. Many attempts have been made to understand the phenomena involved in sintering. Metallic sintering was considered to be a diffusion process¹. The initial stage of sintering² of solids by viscous flow, evaporation and condensation and self-diffusion was also suggested. Sintering was considered to occur by the rearrangement of particles at low temperatures in copper and silver powder^{3,4}. Recently it has also been described as transport of mass⁵. But so far no satisfactory explanation of the mechanism of sintering has been available. It was felt that X-ray diffraction would be useful in studying the problem.

Samples were prepared from copper powder of size 100 μ m obtained from Bharat Metallic Powders Limited, India. The copper powder was pressed in a stainless steel die of the push-pull type. The cylindrical powder pellets were 13.1 mm in diameter. Polyvinyl alcohol was used as binder as it is volatile at about 573 K. The pellets thus prepared were sintered by keeping them in granular petroleum coke powder at temperatures in the range 773 to 1273 K for five different durations of sintering.

X-ray diffraction studies of the sintered samples were done on a Philips P. W. 1730 X-ray diffractometer. In order to study the variation in intensity of diffracted X-rays as a function of temperature parameters like pressure, duration of sintering and the size of the samples were kept constant. Diffractometer parameters like radiation, filter, tube voltage, current, chart speed, scanning rate, time constant, etc were also kept constant. It can be observed from the curve of $I_{(111)}/I_{(200)}$ versus sintering temperature (figure 1) that there is a change in the intensity of reflections with temperature. The (hkl) reflections were found to vary in intensity systematically (table 1). A plot of intensity of X-ray reflections versus sintering temperature is shown in figure 2.

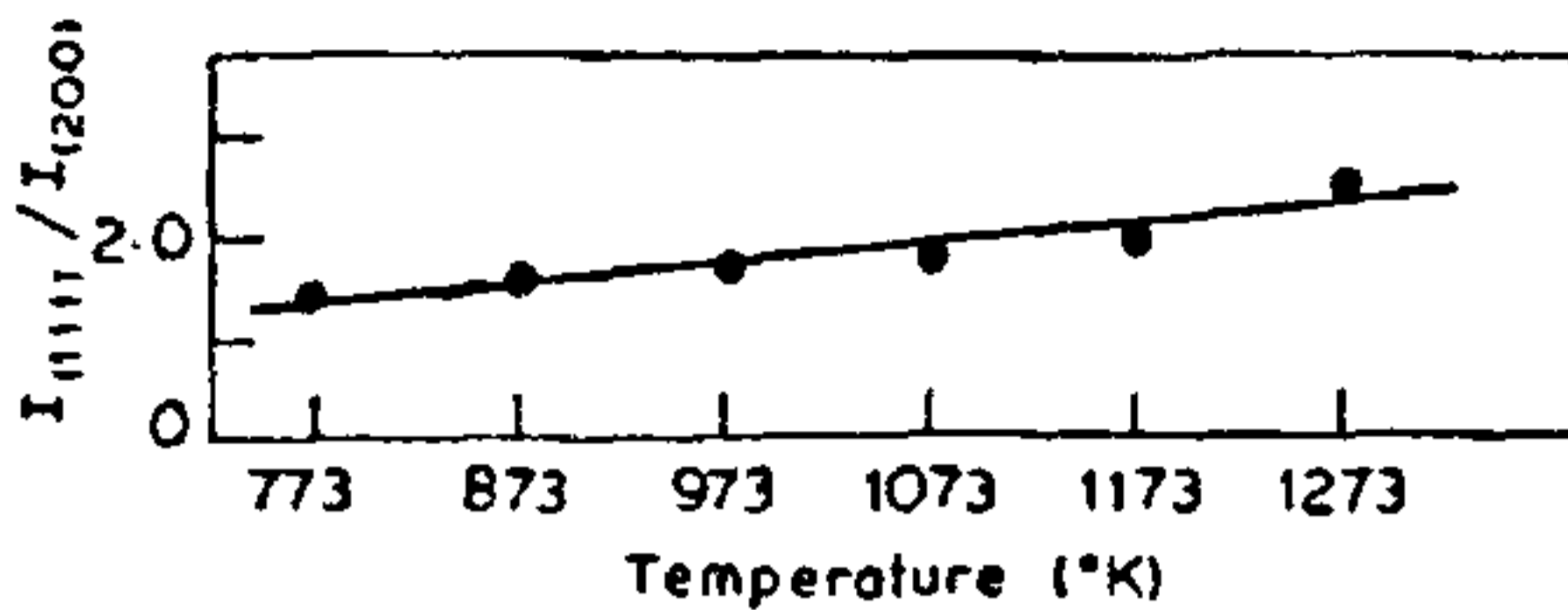


Figure 1. Variation of I_{111}/I_{200} with sintering temperature.

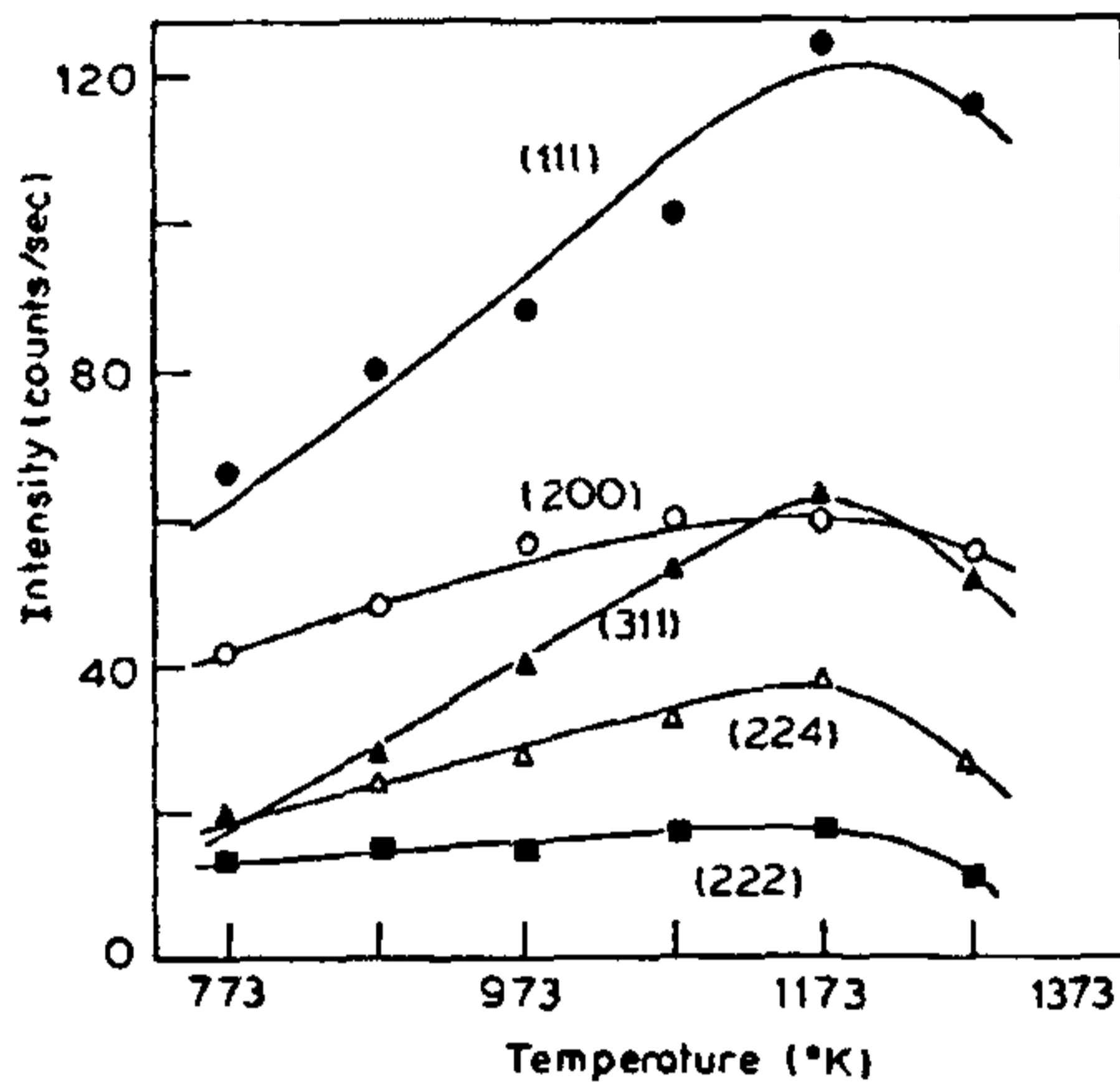


Figure 2. Effect of temperature on the X-ray intensities of different (hkl) reflections.

The intensity of X-ray reflections increases up to 1173 K and beyond this temperature decreases gradually. The increase in intensity was more for the (111), (311) and (220) planes and comparatively less in the case of the (200) and (222) planes. The increase in intensity with increasing sintering temperature

indicates increase in density of the corresponding (hkl) planes of the grains in the compacts.

Three mechanisms have been proposed to contribute densification^{5,6}. But Eadie and Weatherly⁷ have observed the following for copper: (i) If the homologous temperature is <0.75 of the melting point and the neck radius is $<5 \mu\text{m}$, then grain boundary diffusion dominates. (ii) If the homologous temperature is >0.95 of the melting point and the neck radius is $>20 \mu\text{m}$, volume diffusion dominates. The confusion in the literature with regard to the mechanism of sintering was resolved by German and Munir⁶ with reference to the work of Nyce and Shafer⁸: in copper grain boundary diffusion takes place around 1023 K while volume diffusion occurs for compacts of large particles maintained at higher temperatures, around 1123 K. Masuda and Watanabe⁵ concluded that at lower temperatures the grain boundary diffusion contributes to smaller neck sizes and densification. With increase in sintering temperature, the volume diffusion contributes to larger neck size and greater densification. These facts are also reflected in our X-ray intensity observations.

At 773 K and 873 K surface diffusion favours the growth of the neck radius and grain boundary diffusion leads to densification, as revealed by the slight rise in intensity in that interval. Between 873 and 1173 K the appreciable rise in intensity implies increasing densification of the grains due to grain boundary diffusion alone because the surface flow decreases as the neck radius increases and stops finally beyond a critical value of the neck radius. At 1173 K volume diffusion has been confirmed for copper⁹. Thus grain boundary diffusion and volume diffusion contribute to the maximum densification, which is reflected in the maximum intensity at 1173 K in figure 2.

The decrease in intensity beyond 1173 K can be attributed partly to onset of recrystallization. According to Novikov *et al*¹⁰ recrystallization is

Table 1 Intensity of X-ray reflections from sintered samples made of 100 μm Cu powder at 600 MPa pressure after 4 h of sintering

Temperature (K)	Intensity of (hkl) reflections (counts/second)				
	(111)	(200)	(220)	(311)	(222)
773	66	42	20	20	14
873	80	48	25	28	16
973	88	56	28	40	16
1073	100	59	34	52	18
1173	124	60	38	62	18
1273	116	56	28	52	12

also possible during sintering. It is accompanied by a kinetic phenomenon of increased excess vacancy concentration near the melting point. Thus negative shrinkage¹¹ is also a consequence of recrystallization. The decrease in intensity at 1273 K, must be due to the vacancy concentration by recrystallization, which is favoured by the reduction in surface energy at temperatures a little below the melting point.

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A NEW APPARATUS FOR THE DETERMINATION OF GEL STRENGTH OF PHYCOCOLLOIDS

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THE quality of phycocolloids such as agar agar and carrageenan is usually determined by their gel strength^{1,2}. The methods of Nikan Sui and Rower Bal for measuring gel strength are basic controls in the agar market, yet they are not mentioned in the Pharmacopoeias, National Formulary, Codex, or other similar publications or specifications and analytical methods referring to phycocolloids². The principle involved in the determination of gel strength is based on measuring the load (g cm^{-2}) that causes a standard gel (1.5%) to break within a few seconds. In the present attempt a new design for the determination of gel strength has been presented.

A funnel with a basal area of 0.31 cm^2 is attached to a string which is passed over a single fixed pulley. The other end of the string is attached to a weight w . The initial weight of the funnel is p . The weight w should be equal to p . The funnel when initially made to rest on the gel can be considered to be of 'zero' weight as the initial weight p is neutralized by the weight w at the other end of the string (figure 1).

A hot 100 ml of 1.5% solution of phycocolloid was prepared with glass-distilled water and poured into a 500 ml beaker and kept for 24 h at room temperature. The gel was placed under the instrument and the funnel was allowed to rest over the gel. Lead shots were slowly added to the funnel without any disturbance. At a particular weight when the gel was broken, the lead shots were removed and weighed. This weight was divided by the basal area 0.31 cm^2 and expressed as gel strength in g cm^{-2} .

In any ideal machine, the efficiency is equal to unity.

$$\text{Efficiency} = \frac{\text{Mechanical advantage}}{\text{Velocity ratio}}$$

In a simple machine, when the power p just balances the load w , the ratio of the load to the power is called the mechanical advantage, i.e. w/p . In this mechanism the mechanical advantage is unity as w should be equal to p initially.

Let the initial length of the string resting on the gel be L_1 and the length with weight w be L_2 . After the breaking of the gel, the length of the string on