



Fig. 1. The distribution of copper between an aqueous phase and a toluene phase containing various concentrations of cyclohexanone oxime. Initial aqueous concentration of copper, 2 mmol/L.  $\nabla$ , 1.743 mmol/L.;  $\square$ , 1.036 mmol/L.;  $\circ$ , 0.666 mmol/L.;  $\diamond$ , 0.354 mmol/L.;  $\triangle$ , 0.203 mmol/L.

of concentration considered, gives the number of oxime molecules associated with each molecule of extracted complex<sup>4</sup>, namely, about 3.4. It was therefore concluded that the copper complex extracted by cyclohexanone oxime is essentially of the form  $\text{CuA}_4$ , where  $A$  represents the oximate anion, with which slightly more than two other oxime molecules are associated, and in which the copper is monovalent.

Further investigations of these systems are in progress.

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## Transition State in the Inversion of Cyclohexane

CHRISTIANSEN<sup>1</sup> has objected to the "half-chair" conformation ( $C_2$  symmetry) of cyclohexane as the transition form for inversion of the chair conformation (presumably through the twisted boat) as proposed by one of us<sup>2</sup>. Earlier calculations<sup>3</sup> had already indicated that the route through the boat (or twist-boat) form would permit inversion of the chair form of cyclohexane with lower activation energy than that of the planar hexagon.

Christiansen argues that "it is very questionable whether such non-symmetric structures can be formed from the highly symmetrical Sachse hexagon by stressing forces from isotropic surroundings: and finally, if the partition of strain is skew, the internal molecular forces cannot balance each other, as they must". Neither of these objections is valid. Molecules are readily excited to unsymmetrical vibrating states and, eventually, to unsymmetrical transition states by such mechanisms as

absorption of photons or molecular collisions. Indeed, collisions involve obviously anisotropic surroundings. All internal forces of a molecule balance only in an equilibrium configuration. In a vibrating molecule, it is the net force which causes the acceleration in the vibrational motion. Since a transition state is reached by a large amplitude vibration, it is not expected that all internal forces will balance.

Furthermore, Christiansen objects that the two sides of the half-chair form "do not fit", but this objection is only valid if tetrahedral angles are retained on one side of the ring while the other side goes coplanar with  $120^\circ$  angles. In actual fact, of course, in the particular minimum energy half-chair cyclohexane quoted<sup>2</sup>, the bond angles are all altered (within  $C_2$  symmetry), only four carbons are coplanar (only one fully eclipsed bond), and the conformation does represent a closed ring.

Finally, Christiansen concludes that another explanation should be sought for the results of the nuclear magnetic resonance temperature investigations<sup>4</sup> which indicate an activation energy of about 11 kcal/mole for the transition. As these results are consistent with the calculation for the half-chair form and as there is much chemical evidence that the inversion is indeed fast at room temperature, the Baeyer form for the transition state is very unlikely and no re-evaluation of the spectral evidence is required.

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## THE SOLID STATE

### Lattice Contractions in Microcrystals of Nickel-Iron

CONTINUOUS direct recording of electron diffraction patterns as specimens are prepared inside the diffractometer<sup>1,2</sup> increases the sensitivity of observations possible with thin films. Diffraction profiles can be obtained with good signal to noise ratio from films of average thickness equal to a single layer of atoms.

There are two reasons for the improvement in sensitivity. First, the materials are vacuum evaporated in good conditions<sup>3</sup>, with landing parameters up to  $10^6$  Å/sec/torr. Films of the thickness in question, up to 30 Å average value, can rarely be exposed to atmosphere without the danger of oxide forming. Second, the changes on the diffraction profiles are directly observed. The diffraction pattern of the support film is initially recorded, and then successive traces are run as the specimen material is deposited. The material can either be evaporated continuously, in which case thickness alters in the course of recording any given profile, or it can be evaporated in bursts, and the profile measured between each burst. These experimental conditions give similar results in both cases.

Many metals which grow on amorphous substrates have been investigated by this means<sup>3</sup>. Under good vacuum conditions the face-centred cubic metals appear to nucleate by a process of sintering together of minute crystals. At the earliest stages of observation in gold, silver, nickel, 80/20 nickel-iron and lead, the "crystals" contain less than  $\sim 20$  atoms. As the metal is continuously deposited the size of the crystals increases; by the time the average film thickness reaches 20–30 Å, the crystals contain 500 atoms or more, diffraction patterns are similar to those of large crystals (for the range  $1 \leq sa \leq 4$ ,