

agitation chamber A2. Whereas the lower phase returns to the agitation chamber from which it came, the upper phase has been transferred from A to A2. Although the operation has been described stepwise, it is clear that a transfer of the upper phase is obtained by one uninterrupted full turn in the clockwise direction.

Transfer of the lower phase. Steps (1) and (2) of the upper-phase transfer remain unchanged. (3) The horizontal agitation state is attained by turning anti-clockwise for 200°. The two phases flow together through C into the agitation chamber A. The upper phase returns whence it came; the lower phase has been transferred into a direction opposite to the direction of transfer of the upper phase (from A2 to A).

Transfer of the lower phase is obtained by turning 200° in a clockwise direction and back again.

It is obvious that the usual counter-current distribution can also be carried out with this cell.

A train of 216 such cells has been constructed in this laboratory.

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Hydrogen Reduction of Tungsten Oxides

PREVIOUS work¹ has shown that hydrogen reduction of tungsten trioxide gave the β -oxide ($W_{20}O_{58}$)², which was then apparently reduced both to β -tungsten ($\alpha = 5.04$ A.) and to tungsten dioxide or the γ -oxide.

Further work has been done on the reduction of the trioxide, dioxide and γ -oxide. The latter had the composition $W_{18}O_{49.2}$, compared with the stoichiometric composition $W_{18}O_{49}$ ³. 25 mgm. and 50 mgm. samples and a hydrogen flow-rate of 600 c.c./min. were used instead of the 500 mgm. samples and 100 c.c./min. used previously. Reaction products were identified by X-ray diffraction analysis.

The first stage in the reduction of tungsten trioxide was always the formation of β -oxide. The final product was pure β -tungsten at 465°–584° C., but at 645° C. it consisted of α -tungsten and a small amount of the β -form. Samples partially reduced at 465°–645° C. contained only β -oxide and tungsten metal, but the dioxide also was formed at 677° C. and by reduction in moist hydrogen at 645° C.

The final products of reduction of γ -oxide at 470°–584° C. were α - and β -tungsten mixtures, the α -tungsten content increasing with increasing temperature. At 658° C. no β -tungsten was in the final product; but it was present in partially reduced samples. In two samples partially reduced at 470° C. and 540° C. β -tungsten was found unaccompanied by α -tungsten.

The sole product of reduction of the dioxide at 547°–587° C. was α -tungsten.

The following conclusions are reached from this and previous work. The primary product of reduction of tungsten trioxide is β -oxide. β -Oxide is reduced directly to β -tungsten, γ -oxide to both α - and β -tungsten, and the dioxide to α -tungsten.

β -Tungsten is formed from the β - and γ -oxides even at temperatures where it is rapidly converted to α -tungsten. Formation of the γ -oxide and dioxide during reduction of tungsten trioxide is not, as was hitherto thought, a necessary stage in the reaction, but is due to insufficiently rapid removal of water vapour from the reaction zone. The γ -oxide and dioxide may be formed by oxidation of the β -tungsten, or by growth of γ -oxide and dioxide nuclei, formed by oxidation of the primary β -tungsten nuclei.

Only the dioxide was completely reduced to metal. The sigmoid time-course curves for the trioxide flattened out at compositions in the range $WO_{0.2-0.4}$ and at about $WO_{0.98}$ for the γ -oxide. Thus, removal of the oxygen was not quite complete in those cases where β -tungsten was formed. This supports the suggestion of Hägg and Schönberg⁴ that β -tungsten is a metallic oxide, with a maximum oxygen content corresponding to the composition W_3O .

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Quantitative Infra-Red Analysis of Mixtures

DIFFERENTIAL analysis of mixtures is an accepted technique in ultra-violet spectrophotometry¹, and it is the purpose of this communication to describe the successful application of this technique to infra-red solution analysis, where a double-beam instrument is used. Double-beam infra-red spectrophotometers enable complex mixtures of isomeric or closely related substances to be analysed; but it is usually necessary to detect a major peak peculiar to a particular component of the mixture. This is not always possible, and minor peaks, or peaks where interference is present, have been used. In the latter case corrections are applied for the interfering substance, which is separately estimated. Interference can also affect the shoulders adjacent to an analytical peak, so, while the actual peak is unaffected, the resultant extinction coefficient is questionable, because the true base line (I_0 value) is in doubt.

This interference was eliminated by adding to the compensating cell (usually containing solvent only) the interfering substance in a concentration equivalent to that present in the mixture, and dissolved in the solvent used in the sample cell. Alternatively, a different substance having an absorption peak at the same frequency may be used. The resulting trace shows the absorption of the mixture, less that of the interfering substance. Solvent absorption is eliminated by having low concentrations (which may involve thick cells) and using either matched cells or a variable-space cell of thickness similar to that of a fixed-thickness cell. This technique has been used for measuring the percentage of *trans* unsaturated