400. *The Parachor of Rhenium.*

By H. V. A. Briscoe, Percy L. Robinson, and Alfred J. Rudge.

No surface-tension and density data are available from which the parachor of rhenium can be deduced. The attempt now recorded to obtain such data gives an approximate value for the parachor, but, for the reasons stated below, no claim to finality is made, nor will any be possible until appropriate data for compounds other than those employed here are forthcoming.

The present work started with rhenium dioxytrichloride (Briscoe, Robinson, and Rudge, this vol., p. 1104); this was followed by determinations first on rhenium heptoxide and latterly on the trioxymonochloride just discovered by Brukl and Ziegler (*Ber.*, 1932, **65**, 916). Of these preparations, by far the most suitable is the last, which is a colourless mobile liquid at the ordinary temperature and is readily purified by distillation. Rhenium heptoxide may be prepared in a state of high purity, but the working temperatures (above 280°) render the results liable to error. Both of these liquids "wet" glass and their menisci seem to move moderately freely, whereas the dioxytrichloride shows a decided tendency to stick in capillary tubes. For these reasons we attach most value to the results obtained with rhenium trioxymonochloride.

Experimental.

Determination of Surface Tension and Density.—Rhenium dioxytrichloride, ReO_2Cl_3. Re (1·5 g.) was ignited in a mixture of air, about 75%, and Cl at

A (Fig. 1), and the volatile products were condensed in *B*. The apparatus was sealed at *H* and evacuated at *A*; the material was then distilled successively from *C* to *D*, *E*, and *F*. The preparative train was removed by sealing at *I*, and the rest of the apparatus placed in a thermostat. The m. p. of the product was 23·4°. The surface tension was measured by observing with a cathetometer reading to 0·02 mm. the difference in height of the liquid in two capillaries of different and known radii mounted in *F*; the measurements were made at a series of temps., and due regard was paid to the use of falling menisci. Afterwards a suitable amount of the liquid was transferred to the density bulb, which was sealed off at *G*. Measurements of the height of the liquid in the stem of the density bulb were made at various temps., and, subsequent to calibration of vol. by means of H_2O, these were used to ascertain the density over the temp. range. The surface tensions, densities,

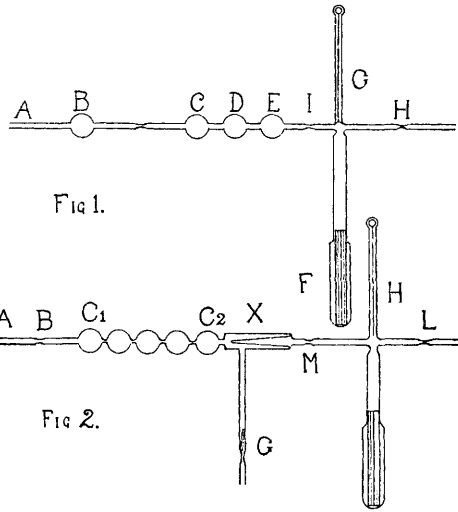

FIG 1.

FIG 2.

and derived parachors are in Table I. In calculating the parachor of Re, besides those for O (2 × 20) and Cl (3 × 54·2), allowance has been made for 2 singlet linkages (— 24·8) and for 2 semipolar double bonds (— 3·2).

TABLE I.

Temp.	$d_4^{t°}$.	γ, dynes/cm.	ΣP.	Parachor of Re.
43°	3·336	46·37	254·3	79·7
44	3·333	45·74	252·2	77·6
44	3·333	46·34	254·5	79·9
47	3·325	46·02	254·6	80·0
51	3·314	43·32	253·0	78·4
59	3·292	42·64	252·3	77·7
				Mean 78·9

Rhenium heptoxide, Re_2O_7. An apparatus similar in form but without bulbs enabled Re to be converted by means of pure dry O into Re_2O_7, which was

eventually sealed up in a vacuum. The residual portion of the apparatus, after removal of the parts used for the prepn., was completely submerged in a molten salt bath (KNO_3 60%, $NaNO_2$ 40%) contained in a well-lagged beaker provided with an observation window, the salt being well stirred and maintained at the required temp. by means of a gas heater. The temp. was observed by means of a chromel–eureka thermocouple used in conjunction with a potentiometer reading to 0·01 mv. The density was determined precisely as described above, a number of observations being made because the parachor is much more affected by the value for the density than by that for the surface tension. The capillary rise was measured at 331°. Values for the density at 331° were found by extrapolation from the various observations, and these, together with the surface tension calc. at 331° and the parachors calc. therefrom, are in Table II. In calculating the parachor of Re, allowance was made for O (7 × 20) and 6 semipolar double bonds (— 9·6).

Table II.

Preptn. 1 : $d_{4^\circ}^{300^\circ}$ 4·458; $d_{4^\circ}^{309^\circ}$ 4·439; $d_{4^\circ}^{328^\circ}$ 4·380; whence $d_{4^\circ}^{331^\circ}$ 4·371.
Preptn. 2 : $d_{4^\circ}^{324^\circ}$ 4·309; $d_{4^\circ}^{334^\circ}$ 4·271; $d_{4^\circ}^{344^\circ}$ 4·234; $d_{4^\circ}^{354^\circ}$ 4·198; whence $d_{4^\circ}^{331^\circ}$ 4·373.
Preptn. 3 : $d_{4^\circ}^{308^\circ}$ 4·322; $d_{4^\circ}^{318^\circ}$ 4·271; $d_{4^\circ}^{320^\circ}$ 4·250; $d_{4^\circ}^{327^\circ}$ 4·234; $d_{4^\circ}^{332^\circ}$ 4·193; $d_{4^\circ}^{338^\circ}$ 4·170; $d_{4^\circ}^{340^\circ}$ 4·163; whence $d_{4^\circ}^{331^\circ}$ 4·198.
Preptn. 4 : $d_{4^\circ}^{303^\circ}$ 4·432; $d_{4^\circ}^{312^\circ}$ 4·361; $d_{4^\circ}^{328^\circ}$ 4·287; whence $d_{4^\circ}^{331^\circ}$ 4·262.

Preptn.	γ_{331°, dynes/cm.	ΣP.	Parachor of Re.	Preptn.	γ_{331°, dynes/cm.	ΣP.	Parachor of Re.
1	32·77	265·0	67·3	3	31·47	273·1	71·4
2	32·78	264·8	67·2	4	31·96	270·0	69·8
						Mean	68·9

Rhenium trioxymonochloride, ReO_3Cl. This compound (Brukl and Ziegler, *loc. cit.*) was prepared in the apparatus (Fig. 2) by heating about 3 g. of metallic Re at *A* alternately in O and in Cl in such a manner that a small quantity of Re_2O_7 was driven into C_1 and there subsequently mixed with a deficiency of ReO_3Cl. This mixture was then heated and distilled from bulb to bulb until it was eventually collected at C_2. This process was repeated until all the metal had been converted and transferred to C_2. As this, in common with the other compounds employed in this research, is hygroscopic and decomp. by H_2O, the apparatus was previously carefully dried, and the gases employed were passed over P_2O_5 before entering the apparatus. In spite of all precautions, slight reduction to a blue compound took place in the course of the prepn., and as this tended to be distributed over the walls of the apparatus, thereby fouling the surface-tension tubes, a 'special' joint was introduced at *X*. After the preparative work was completed, the apparatus was sealed at *G*, evacuated at *A*, and sealed at *B*; then the portion beyond the 'special' joint was evacuated and sealed at *L*. The seal between the two portions was broken, and the compound distilled into *I* by immersing that vessel in a solid CO_2–EtOH freezing mixture. The product was a colourless liquid, and the walls of the density–surface tension vessel were free from stain. After sealing at *M*, measurements were taken from which the results in Table III are derived. In calculating the parachor of Re, allowance was made for O (3 × 20), Cl (54·2), and 3 semipolar double bonds (— 4·8).

TABLE III.

Prep. No.	Temp.	d_4°.	γ, dynes/cm.	ΣP.	Parachor of Re.
1	19°	3·834	49·04	186·4	77·0
2	16	3·878	51·23	186·0	76·6
2	20	3·867	50·28	185·6	76·2
2	29	3·826	48·44	185·8	76·4
2	34	3·819	47·58	185·4	76·0
2	36	3·800	46·96	185·7	76·3
2	37	3·781	46·22	185·9	76·5
					Mean 76·4

DISCUSSION.

The mean values for the parachor of rhenium derived from the above compounds, *viz.*,

Compound.....	ReO_2Cl_3	Re_2O_7	ReO_3Cl
Parachor of Re	78·9	68·9	76·4

show a reasonable agreement between the values derived from these two oxychlorides and a lower result from the oxide. Most significance is attached to the parachor from the trioxychloride. The maximum result, 78·9, is of the order anticipated from the values ascribed to tungsten (90) and osmium (75) (Sugden, "The Parachor and Valency," p. 189): the mean, 74·6, is decidedly lower than this, but admittedly the values for tungsten and osmium are very rough.

Acknowledgment is made of a grant from the Research Committee of this College for the purchase of rhenium.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, August 12th*, 1932.]