NOTES.

The Parachor of Hydrogen Bromide. By THOMAS G. PEARSON and PERCY L. ROBINSON.

THE surface tension and density of liquid hydrogen bromide as determined by McIntosh and Steele (*Proc. Roy. Soc.*, 1904, **73**, 450) differ markedly from the values anticipated from the corresponding data for the hydrides of chlorine and iodine (see this vol., p. 739). In particular, their value for the surface tension at the b. p. is higher than that of hydrogen iodide at its b. p. We have determined these two constants, and our results agree well with the anticipated figures; an error in the earlier density measurement was responsible for the erroneous value of surface tension.

Hydrogen bromide, prepared by the action of bromine vapour on excess of hydrogen in the presence of platinised asbestos, was condensed in liquid air and fractionated in a vacuum. The determination of surface tension was effected by capillary rise, and that of density in a Pyrex pyknometer, the apparatus and procedure being identical with that previously described (Durrant, Pearson, and Robinson, this vol., p. 732). The results, together with the parachors calculated therefrom, are recorded in the table, wherein D = liquid density, d = vapour density, h = difference in level of the liquid in the capillaries, $r_1 = 0{\cdot}27165$ mm., $r_2 = 0{\cdot}49920$ mm., $g = 981{\cdot}45$, γ = surface tension $= r_1 r_2 g(3h + r_2 - r_1)(D - d)/6(r_1 - r_2)$, P = parachor $= \gamma^{\frac{1}{4}} M/(D - d)$.

Temp.	HBr, wt. (g.).	HBr, vol. (c.c.).	*D*, g./c.c.	*d*, g./c.c.	*h*, cm.	γ, dynes/cm.	*P*.
− 67·1°	1·8372	0·8087	2·717	0·005	0·416	27·07	81·39
− 60·0	1·8372	0·8210	2·238	0·007	0·399	25·54	81·53
− 46·0	1·8372	0·8449	2·174	0·012	0·366	22·67	81·86

From the data, the coefficient of expansion between − 67·1° and − 46° = 0·002119, the temperature coefficient of surface tension = 0·2085 dyne/cm./degree, and the Ramsay–Shields constant $d[(Mv)^{\frac{2}{3}}\gamma]/dt = 1{\cdot}91$, showing that the liquid is, at most, but slightly associated.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, April 26th,* 1934.]

The Colour Changes in Light and Darkness of Ammonium Thiocyanate Solutions. By BH. S. V. RAGHAVA RAO.

THE reversible changes of colour which a concentrated aqueous solution of ammonium thiocyanate undergoes in light and in darkness have formed the subject of a number of communications. These are reviewed by Sharma (J., 1930, 308), who agreed that traces of iron are essential for the changes, but put forward the view that an oxygen complex of ferric thiocyanate of unknown composition is formed during the light reaction. In view of the conflicting evidence, it seemed desirable to reinvestigate the phenomenon, and the following experiments show it to be due to reversible oxidation–reduction processes involving iron present as impurity.

1. The changes are not shown by carefully purified ammonium thiocyanate.

2. A solution of the salt which is insensitive to light may be made active by the addition of 0·0033 mg. of iron per l., but such a solution is not rapidly decolorised in the dark. Rapid decoloration is effected by addition of small quantities of heavy metals, *e.g.*, lead, manganese (?), and especially mercury; addition of sulphurous acid or mere boiling of the solution also accelerates decoloration in the dark.

3. In active samples of the substance the presence of iron may be proved by reaction with dimethylglyoxime, which gives a faint but detectable rose-red coloration with 1 part of iron in 10^8 parts.

4. The coloration proceeds only in the presence of oxygen; nitrogen and carbon dioxide greatly retard or entirely inhibit it.

5. Nitric acid, hydrogen peroxide, and ozone produce the coloration in the absence of light.

6. The colour may be extracted with ether or amyl alcohol.

7. Identical absorption spectra are shown by a dilute solution of ferric thiocyanate and by solutions of the ammonium thiocyanate whether initially active or rendered so as in (2) above.

8. Fatigue effects are not present: repeated insolation and keeping in the dark does not impair the activity of the solution.

9. The coloration proceeds equally well in glass and in silica vessels. Light of wave-lengths below 500 $\mu\mu$ is active (maximum at **360**—450 $\mu\mu$), but light of longer wave-length accelerates the decoloration.

10. Preliminary experiments on the rate of coloration in the total radiation from a 100 c.p. Pointolite lamp have shown that the coloration proceeds linearly with time of exposure at first; the relationship then becomes more complicated and this is being further investigated. The linear relationship is maintained for longer if the solution is stirred, showing that the complexity arises in part from the absorption of the active radiation by the coloured solution. The rate of coloration is also proportional to the intensity of the incident light.

Expts. 1, 2, and 3 show that the presence of iron is necessary for the exhibition of the colour changes. Expts. 4 and 5 further show that the coloration is an oxidation process, thermal or photochemical, and the decoloration is a dark reduction process. Expts. 6 and 7 indicate that the colouring matter is ferric thiocyanate.

Sharma rejected the view that the colour was due to ferric thiocyanate on the grounds that this substance " is decolorised neither by heating nor by keeping in the dark; moreover, it is bleached by light." His hypothesis was advanced solely because, in general, ferric salts are known to be reduced by the action of light, but this effect may be reversed in the presence of more easily reducible substances; and Winther (*Z. Elektrochem.*, 1912, **118**, 138) has shown that in the presence of mercuric chloride ferrous salts are oxidised, the reverse reaction taking place in the dark.—ANDHRA UNIVERSITY, WALTAIR, S. INDIA. [*Received, March 26th*, 1934.]