"On the Liquefied Hydrides of Phosphorus, Sulphur, and the Halogens, as Conducting Solvents.—Part I." By D. McIntosh and B. D. Steele. Communicated by Sir William Ramsay, K.C.B., F.R.S. Received April 26,—Read May 19, 1904.

Ammonia, water, and hydrofluoric acid, are the only hydrides of the elements which have been systematically investigated with respect to their solvent properties, and in particular with respect to their power of forming electrically conducting solutions. With the object of extending our knowledge of the properties of these hydrogen compounds, when liquefied, and in the hope that more light might thereby be thrown on the question of ionic dissociation, the investigation, of which this is a brief abstract, has been undertaken.

The following hydrides of the fifth, sixth, and seventh groups have been examined, hydrogen phosphide, sulphide, chloride, bromide, and iodide. Since it had been found by preliminary experiments that, with the exception of hydrogen phosphide, all these possessed the power of conducting the current when certain substances were dissolved in them, a number of physical constants were measured before proceeding to the systematic study of the conductivity of solutions.

A brief summary of the results found hitherto is contained in the following tables, in which the temperatures are given to the nearest tenth of a degree.

1.—*The Vapour Pressure Curves.*

These were determined by the method described by Travers, Senter, and Jaquerod,* and used by them for the measurement of the vapour pressures of liquid oxygen and hydrogen.

Hydrochloric Acid.

T.	P.	T.	P.	T.	P.
−109·9	141·0	−97·2	316·0	−85·9	648
−104·5	198·0	−92·9	430·0	−83·2	748
−101·3	245·0	−89·8	522·0	−80·5	868

Hydrobromic Acid.

T.	P.	T.	P.	T.	P.
−104·2	96·0	−89·3	245·0	−76·7	501
−100·7	142·0	−87·1	284·0	−74·0	575
−96·3	185·0	−83·0	357·0	−70·7	682
−92·8	214·0	−79·3	431·5	−68·4	775

* 'Phil. Trans.,' A, 1902, vol. 200, p. 138.

Hydriodic Acid.

T.	P.	T.	P.	T.	P.
−77·9	74·0	−54·8	303·5	−43·5	530
−73·5	92·0	−51·4	369·0	−41·7	578
−68·4	126·0	−50·0	376·0	−39·4	644
−63·5	185·5	−47·7	438·0	−36·9	713
−59·5	224·0	−46·1	474·0	−35·9	769

Sulphuretted Hydrogen.

T.	P.	T.	P.	T.	P.
−84·0	193·0	−75·6	314·0	−69·1	456
−81·7	220·0	−73·3	364·0	−66·1	538
−78·4	270·0	−71·6	400·0	−62·2	676

Phosphoretted Hydrogen.

T.	P.	T.	P.	T.	P.
−105·9	237·0	−97·7	393·0	−88·6	644
−101·2	319·0	−93·1	498·0	−86·6	719

The melting and boiling points as read from the curves are as follows :—

	HCl.	HBr.	HI.	H_2S.	H_3P.
M. p.	—	−86·0	−50·8	—	—
B. p.	−82·9	−68·7	−35·7	−60·1	−86·2

2.—*The Densities.*

The densities of the pure liquids were determined over a wide range of temperature, and the values at the boiling point are given in the following table :—

	HCl.	HBr.	HI.	H_2S.	H_3P.
Density at b. p.	1·195	2·157	2·799	0·964	0·744

3.—*The Molecular Surface Energy.*

The surface energies were measured over a considerable range of temperature, using a modification of the method of Ramsay and Shields. In the table the value of the molecular surface energy $\lambda(MV)^{\frac{2}{3}}$ at various temperatures is given. The values of $d\lambda(MV)^{\frac{2}{3}}/dT$ and of the association factor x are tabulated separately. From the results it will be seen that of the substances examined, hydrogen, bromide, iodide, and sulphide occur as simple molecules; whilst hydrogen chloride and phosphide are more or less associated.

Hydrochloric Acid.

T.	$\lambda (MV)^{\frac{2}{3}}$.	T.	$\lambda (MV)^{\frac{2}{3}}$.	T.	$\lambda (MV)^{\frac{2}{3}}$.
163·1	263·7	175·8	244·8	187·2	229·3
168·5	255·9	180·1	239·0	189·9	223·6
171·8	250·8	183·2	233·6	192·6	221·0

Hydrobromic Acid.

181·9	330·1	188·9	314·6	198·2	294·8
184·8	325·6	193·4	307·3	200·5	292·2
186·1	320·1	195·3	299·6	203·9	283·8

Hydriodic Acid.

225·3	367·0	230·9	355·3	235·0	348·0
227·1	362·8	232·9	351·0	236·5	344·6
229·3	358·5	—	—	—	—

Sulphuretted Hydrogen.

189·1	349·5	197·4	334·1	203·9	324·7
191·3	345·3	199·7	328·3	206·9	316·7
194·6	338·0	201·5	326·6	210·8	308·6

Phosphoretted Hydrogen.

167·1	287·2	175·4	273·4	—	—
171·8	279·6	179·9	265·4	—	—

Variation of molecular surface energy with temperature and the association factor—

	HCl.	HBr.	HI.	H_2S.	H_3P.
$d\lambda (MV)^{\frac{2}{3}}/dT$...	1·47	2·03	1·99	1·91	1·70
x.................	1·5	1·0	1·0	1·1	1·4

4.—*The Viscosities, and Viscosity Temperature Coefficient.*

The viscosities of the pure liquids were determined by comparison with that of distilled water at 22°. The object of the measurements was to procure data for the comparison of the temperature coefficients of viscosity and of electrical conductivity.

Viscosity Temperature Coefficient, $d\eta/dT$.

Hydrochloric Acid.

T	160·8	166·7	171·7	177·0	183·2	188·2
η.........	0·590	0·569	0·530	0·514	0·493	0·477

$$d\eta/dT = 0·88.$$

Hydrobromic Acid.

T	186·8	188·8	190·8	193·7	197·3	199·4
η.........	0·911	0·902	0·890	0·877	0·857	0·851

$$d\eta/d\mathrm{T} = 0{\cdot}57.$$

Hydriodic Acid.

T	223·3	225·6	227·2	230·6	231·5	233·9	236·4
η......	1·479	1·454	1·437	1·426	1·402	1·377	1·353

$$d\eta/d\mathrm{T} = 0{\cdot}70.$$

Sulphuretted Hydrogen.

T	191·0	193·3	198·2	201·2	206·1	209·8
η.........	0·547	0·528	0·510	0·488	0·470	0·454

$$d\eta/d\mathrm{T} = 1{\cdot}10.$$

5.—*Solubilities and Conductivities.*

Of the substances examined at this stage, the organic ammonium salts were found to be readily soluble, and to give conducting solutions. Some doubt existed as to whether any metallic salts were dissolved; if so, none were found to conduct the current. The only readily soluble inorganic substances were hydrogen chloride and bromide dissolved in sulphuretted hydrogen. It is somewhat remarkable that these solutions are perfect non-conductors.

The conductivity of a few substances was accurately determined; as, for instance, that of solutions of triethyl ammonium chloride in hydrogen bromide and sulphide. It was found that the molecular conductivity of these two solutions, and of all the others which were examined, increased enormously with increasing concentration, instead of showing a slight decrease, as in the case of aqueous solutions.

The further study of the solubilities and conductivities forms the subject of another paper.*

* *Infra*, p. 454.