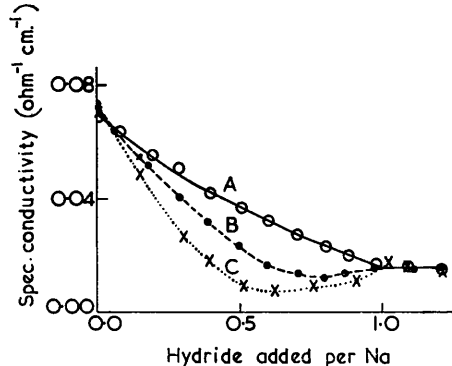




minimum and changed sharply to clear yellow at an arsine : sodium ratio of unity. These results are similar to those for stannane,<sup>1</sup> and suggest that both  $\text{AsH}_2\text{Na}$  and  $\text{AsHNa}_2$  were formed in the early stages of the titration and that, in its later stages, the reaction  $\text{AsHNa}_2 + \text{AsH}_3 \rightarrow 2\text{AsH}_2\text{Na}$  occurred. Various other mechanisms were considered but the foregoing seems the most probable and is supported by measurements of the hydrogen evolution (Fig. 2). In the early stages of the titration about 1.4 atoms of hydrogen were evolved for each molecule of arsine added, corresponding to a 40% formation of  $\text{AsHNa}_2$ . The hydrogen evolution fell off as the titration proceeded and was very slight towards the end. The overall reaction ratio was one atom of hydrogen per molecule of hydride. Arsine differs from stannane and germane (see below) in continuing to evolve hydrogen beyond the conductivity minimum, showing that some  $\text{AsH}_2\text{Na}$  was formed directly throughout.

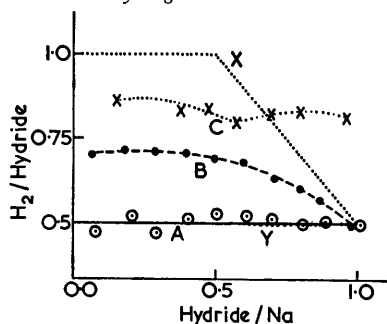
Results for stibine at  $-63.5^\circ$  were less reproducible because of its lower stability, but they showed it to behave in a similar manner to arsine. Fig. 1 shows a steeper fall in conductivity and a minimum at a smaller hydride : sodium ratio than in the case of arsine,

FIG. 1. The titration of the Group V hydrides: the variation in specific conductivity at  $-63.5^\circ$ .



A, Phosphine against 15.8 mg. of sodium in 2.30 ml. of ammonia. B, Arsine against 24.9 mg. of sodium in 3.29 ml. of ammonia. C, Stibine against 19.2 mg. of sodium in 2.89 ml. of ammonia.

FIG. 2. The titration of the Group V hydrides: hydrogen evolution.



A, B, C as in Fig. 1. X, Y, evolution expected from complete formation of the disodium or monosodium derivative respectively.

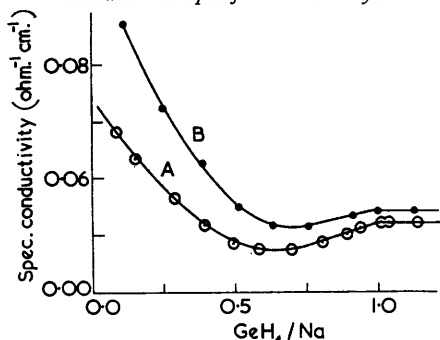
indicating a greater tendency to form the disodium derivative  $\text{SbHNa}_2$ . Evolution of hydrogen was also greater in the early stages though observations towards the end of the reaction were vitiated by decomposition, which led to deposition of a thin film of antimony on the reaction vessel above the liquid surface. The blue colour of the solution changed to dark green as the titration proceeded and this intense colour was discharged at a stibine : sodium ratio of approximately 1, leaving an orange solution. The essential data for the three hydrides are summarised here in a Table. These figures give the values for four runs with each hydride, except for the stibine values at the end point (a), which were taken from the two runs where decomposition was least.

Hydride	Molar ratio Hydride : sodium		Hydrogen : hydride
	at min.	at end-point	
$\text{PH}_3$ .....	—	$0.98 \pm 0.03$	$0.50 \pm 0.01$
$\text{AsH}_3$ .....	$0.83 \pm 0.04$	$1.00 \pm 0.03$	$0.49 \pm 0.02$
$\text{SbH}_3$ .....	$0.66 \pm 0.05$	$1.02$ (a)	$0.53$ (a)

The results for titrations with monogermane at  $-63.5^\circ$  are shown in Fig. 3. The conductivity curve was similar to that for stannane, but the minimum was shallower and

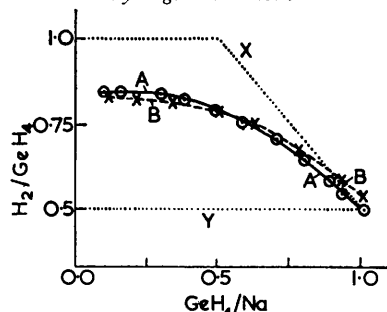
occurred at a higher hydride:sodium ratio. The blue colour was discharged at the minimum, leaving a pale yellow solution and a yellow-green precipitate. This precipitate dissolved almost completely on further additions of hydride up to a 1:1 ratio; it was not isolated, but was probably the disodium derivative. The hydrogen evolution in the monogermene titration is shown in Fig. 4. In the early stages approximately 1.6 atoms of hydrogen were evolved per molecule of hydride added. The overall molecular ratio of hydrogen to hydride was 0.52 and 90—95% of the total hydrogen had been evolved by the time the conductivity minimum was reached. These results support strongly the hypothesis that the disodium derivative is first formed in this case also. The slight excess of hydrogen probably arises from ammonolysis of the monogermene, which is known to occur but is much slower than that of monosilane (see below). The variation in the

FIG. 3. The titration of monogermene: the variation in specific conductivity.



A, Monogermene against 20.2 mg. of sodium in 3.66 ml. of ammonia at  $-63.5^{\circ}$ . B, Monogermene against 19.0 mg. of sodium in 3.40 ml. of ammonia at  $-45^{\circ}$ .

FIG. 4. The titration of monogermene: hydrogen evolution.



A and B, as in Fig. 3. X and Y, as in Fig. 2.

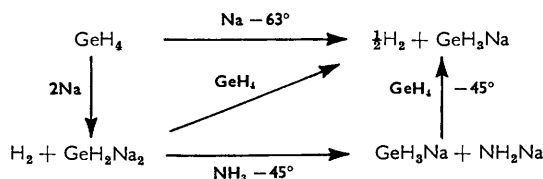
position of the minimum and of the end point in a series of experiments is shown in the Table.

Wt. of Na (mg.-atoms)	Concn. of Na solution (M)	GeH <sub>4</sub> : Na		Total H <sub>2</sub> : GeH <sub>4</sub>
		At min.	At end-point	
0.684	0.175	0.72	1.04	0.53
0.908	0.246	0.80	0.99	0.53
0.893	0.241	0.69	1.02	0.51
0.878	0.238	0.71	0.98	0.52
0.844	0.238	0.70	1.08	0.53

In preliminary work on the effect of temperature on this reaction, observations were made at  $-45^{\circ}$ . After an increment of hydride had been added at this temperature and thermal equilibrium had been reached, the conductivity became constant at one value (A) for 2—3 min. and then rose during about 3 min. to a higher value (B). An example of this was a rise in specific conductivity from 0.0804 (A) to 0.0966  $\text{ohm}^{-1} \text{cm}^{-1}$  (B). This effect was reproducible and occurred in each titration until the free sodium had been used up. It was not observed at  $-63.5^{\circ}$  and suggests that a second reaction occurred after the initial reaction of the hydride with the sodium solution.

A titration curve at  $-45^{\circ}$ , plotted with the final conductivities, B, is shown in Fig. 3. The hydrogen evolution is shown on Fig. 4. Results at the two temperatures are very similar except that the minimum comes at a higher hydride:sodium ratio at the higher temperature. The same overall reaction appears to occur at the two temperatures, but the mechanism may be different. If it involved the solvent at the higher temperature, as shown, the rise in conductivity (A to B) could be interpreted as due to replacement of the

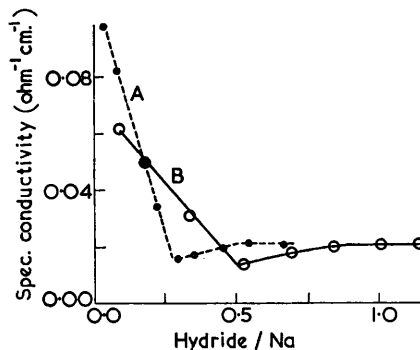
germylene dianion by the germyl anion and the more mobile solvent anion. Monogermene is known to react with sodamide in the manner indicated.<sup>4</sup>



It is relevant to the experiments with di- and tri-germane that Kraus and Carney,<sup>5</sup> in preparing monogermene by the acid-decomposition of magnesium germanide in liquid ammonia, removed higher hydrides from their product by treatment with a solution of sodium in ammonia. The products of this reaction were assumed to be  $\text{GeH}_3\text{Na}$  and  $\text{GeH}_2\text{Na}_2$ , formed by fission of the Ge-Ge bonds. They gave monogermene on treatment with an acid. The titration curve for digermene (Fig. 5) shows a sharp break at a reactant ratio of 0.5; at that point the colour of the solution also changed sharply from blue to pale green. This is the behaviour expected for the reaction  $\text{Ge}_2\text{H}_6 + 2\text{Na} \rightarrow 2\text{GeH}_3\text{Na}$  postulated by Kraus and Carney. However, hydrogen was evolved up to the 0.5 ratio in amounts proportional to the size of the hydride increment. The total amount

FIG. 5. The titration of the higher germanes: the variation in the specific conductivity at  $-63.5^\circ$ .

A, Digermene against 15.1 mg. of sodium in 3.32 ml. of ammonia. B, 171 mg. of tri-germane against excess of sodium in 2.97 ml. of ammonia.



was small and fell as the initial concentration of the sodium solution was increased. Thus, for a 1.82M-sodium solution a total of 0.18 atom of hydrogen per digermene molecule was obtained, while for 0.22M- and 0.12M-solutions the amounts were 0.22 and 0.46 atom, respectively. The position of the conductivity break was independent of the hydrogen evolved and this suggests that a second reaction, such as  $\text{Ge}_2\text{H}_6 + 2\text{Na} \rightarrow \text{Ge}_2\text{H}_4\text{Na}_2 + \text{H}_2$ , occurs as well as that postulated by Kraus and Carney.

The curve for trigermane (Fig. 5) shows a minimum at a reactant ratio of 0.25, at which point the colour changed from blue to dark red. The conductivity rose between the 0.25 and the 0.5 ratios. The total hydrogen evolved in the titration, which was not carried to completion because of lack of material, was 0.201 mmole for 0.756 mmole of hydride. The ratio of hydrogen to hydride at the minimum was approximately 0.4, and at the 0.5:1 ratio had fallen to 0.3. This preliminary experiment shows that the reaction, which up to the minimum might be represented as  $\text{Ge}_3\text{H}_8 + 4\text{Na} \rightarrow 2\text{GeH}_3\text{Na} + \text{GeH}_2\text{Na}_2$ , was in fact more complicated.

From these results for the various hydrides examined, the extent to which a disodium derivative is formed increases as the central atom becomes more electropositive. On this basis monosilane would show a minimal tendency to form a disodium derivative with the

<sup>4</sup> Glarum and Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 5399.

<sup>5</sup> Kraus and Carney, *J. Amer. Chem. Soc.*, 1934, **56**, 765.

alkali metals. Addition of this hydride to a solution of sodium in ammonia led to a steady decrease in conductivity up to a hydride : sodium ratio of about 0.37. Beyond this point conductivity measurements were not reproducible and the hydrogen evolution increased considerably. The infrared spectrum of the solid left after removing ammonia showed no absorption at  $2150\text{ cm.}^{-1}$  (Si-H stretch frequency), but a strong band at  $3300\text{ cm.}^{-1}$  (N-H stretch), proving that complete solvolysis had occurred. To overcome this difficulty the reaction of monosilane with a solution of potassium in diethylene glycol dimethyl ether was examined. Addition of an excess of monosilane discharged the blue colour with evolution of hydrogen. Addition of methyl iodide to the product gave 1.42 mmoles of methylsilane from 1.46 mmoles of silane. This observation, which is being further studied, proves that silylpotassium can be formed when solvolysis does not occur, though it gives no indication of the rôle of silylenepotassium in the reaction.

#### EXPERIMENTAL

Phosphine, arsine, and monosilane were prepared by standard methods. Stibine was prepared by adding a slight excess of sodium borohydride rapidly to partially hydrolysed antimony trichloride in water at  $20^\circ$ . The hydride evolved was readily separated from water by distillation at  $-85^\circ$  (yield 95%) in contrast to its difficult separation from ether when lithium aluminium hydride was used as a reducing agent (Found:  $M$ , 125. Calc. for  $\text{H}_3\text{Sb}$ :  $M$ , 125). The infrared spectrum was identical with that recorded in the literature.<sup>6</sup> The germanes were prepared by acid-hydrolysis of magnesium germanide;<sup>7</sup> the best yields (*ca.* 27%) were obtained with germanide prepared by heating stoichiometric amounts of the finely powdered elements in hydrogen at  $750\text{--}800^\circ$  (24 hr.); the product was added fairly rapidly to 50% phosphoric acid at  $50^\circ$ ; the hydrides  $\text{GeH}_4$ ,  $\text{Ge}_2\text{H}_6$ , and  $\text{Ge}_3\text{H}_8$  were obtained in the approximate ratio 9 : 4 : 1 and were separated by vacuum-fractionation and characterised by their molecular weights, vapour pressures, and infrared spectra (for  $\text{GeH}_4$  and  $\text{Ge}_2\text{H}_6$ ). The infrared spectrum of trigermane, which has not been recorded, showed strong absorption bands at 2080 and  $801\text{ cm.}^{-1}$  (with shoulders at 810 and  $820\text{ cm.}^{-1}$ ). The trigermane used was estimated, from its absorption spectrum, to contain about 4% of digermane.

The apparatus and technique used in the conductimetric titration were similar to those used in the experiments on stannane.<sup>1</sup> The amounts of hydride added in the titrations were measured manometrically in a bulb of known volume, by direct weighing, or by a combination of these methods, depending on the stability of the compound and its solubility in tap grease. Conductivities were measured at  $-63.5^\circ$  in a bath of melting chloroform.

*Reaction of Monosilane with Potassium in Diethylene Glycol Dimethyl Ether.*—When an excess of monosilane was added to a solution of potassium in the ether of unknown concentration the blue colour was discharged. The unchanged hydride was separated and measured. It was found that 1.46 mmoles of monosilane yielded 0.718 mmole of hydrogen. An excess of methyl iodide was added to the solution. The volatile product was removed and separated from methyl iodide and solvent by distillation at  $-63.5^\circ$ . It was methylsilane (1.42 mmoles) (Found:  $M$ , 43. Calc. for  $\text{CH}_3\text{Si}$ :  $M$ , 46); the identity was checked by the infrared spectrum.<sup>8</sup>

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UNIVERSITY CHEMICAL LABORATORY,  
LENSFIELD ROAD, CAMBRIDGE.

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<sup>6</sup> Smith, *J. Chem. Phys.*, 1951, **19**, 384.

<sup>7</sup> Dennis, Corey, and Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657.

<sup>8</sup> Kaye and Tannenbaum, *J. Org. Chem.*, 1953, **18**, 1751.