

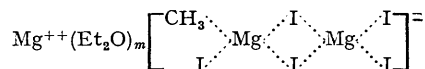
### 558. Thermodynamics of Grignard Compounds: Equilibria in the System $\text{CH}_3\text{MgI}-\text{MgI}_2-(\text{C}_2\text{H}_5)_2\text{O}$ .

By R. STEWART and A. R. UBBELOHDE.

Possible equilibria in a system containing methylmagnesium iodide, magnesium iodide, and diethyl ether have been studied in sealed vessels, by evaluating the concentration of magnesium iodide from freezing-point data. Observed results can be accounted for on the basis of an equilibrium



in which the complex probably has the structure

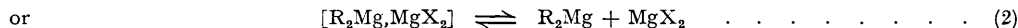


Equilibrium is attained rapidly. Previous observations on slow equilibria are discussed.

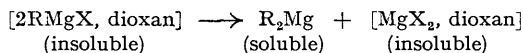
The heat of formation of the complex ( $-18.3$  kcal./mole) is comparable with that of  $\text{Al}_2\text{Cl}_6$  ( $-22.5$  kcal./mole). Complex formation may tentatively be attributed to similar forces.

The solubility curve of magnesium iodide dietherate in ether has been redetermined from  $0^\circ$  to  $20^\circ$ . The heat of solution is  $14.7$  kcal./mole, if deviations from ideal solutions are neglected.

PUBLISHED evidence about the molecular state of Grignard compounds in ethereal solution is conflicting. Molecular-weight determinations (see Discussion, below) indicate the presence, in solution, of molecules containing more than one magnesium atom. Differential precipitation with dioxan has been used to assess concentrations of halogen-magnesium compounds in possible equilibria such as



where R is an alkyl or aryl group and X is a halogen atom, and the results have been interpreted in favour of equation (1) (Schlenk and Schlenk, *Ber.*, 1929, **62**, 920). However, the precipitation method assumes that the time required for a shift of equilibrium is large compared with the time required for formation and analysis of the precipitates, in view of complications from slow processes such as



Various observations on the effects of time on the composition of the precipitates indicate that the interpretation of precipitation results is not straightforward (Cope, *J. Amer. Chem. Soc.*, 1935, **57**, 2238; 1938, **60**, 2215; Noller and White, *ibid.*, 1937, **59**, 1354).

A further complication is that atmospheric oxidation may seriously affect the apparent position of equilibrium (Noller and Raney, *ibid.*, 1940, **62**, 1749; Noller and Castro, *ibid.*, 1942, **64**, 2509). It seems evident that very rigorous precautions must be taken to obtain satisfactory physico-chemical measurements on these systems.

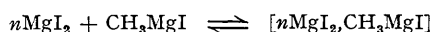
Another line of inquiry arose from observations that the solubility of magnesium chloride in ether is greatly *increased* by the presence of the Grignard compounds. This cannot be explained in terms of equations (1) and (2). It was originally attributed to the production of metastable supersaturated solutions of magnesium chloride during the formation of the Grignard compound (Schlenk and Schlenk, *loc. cit.*). However, the increased solubility has since been observed in the presence of solid magnesium chloride (Doering and Noller, *J. Amer. Chem. Soc.*, 1939, **61**, 3436).

A fourth line of evidence has been obtained from studies of the electrolysis of organo-magnesium halides (cf. Evans, Pearson, and Braithwaite, *ibid.*, 1941, **63**, 2574, who give earlier references). Transference studies indicate that magnesium must be present in the anions as well as in the cations, which again does not agree with equations (1) and (2) (see Discussion, below).

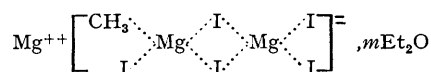
The object of the present investigation was to obtain more precise information about the equilibria in Grignard solutions. Really reliable determinations of equilibrium constants for reactions such as (1) and (2) would be of great interest in leading to standard free energies related to thermochemical data on Grignard compounds (Mackle and Ubbelohde, *J.*, 1948, 1161; Mackle, Maniece, and Ubbelohde, unpublished).

Sealed vessels were prepared containing varying amounts of ether, magnesium iodide, and methylmagnesium iodide. In the light of previous experience rigorous precautions were taken to avoid atmospheric oxygen and other impurities. It was also found necessary to eliminate photochemical effects by working in the dark. The concentration of magnesium iodide in a vessel was determined from time to time over a period of days, using a simple freezing-point technique, and the concentration of the other components was evaluated by difference.

No evidence could be obtained of an equilibrium of the Schlenk type. As is discussed below, the observations could be accounted for in terms of the formation of a complex, which may in addition contain ether molecules :



The most probable values are  $n = 2$ , and the heat of formation =  $-18.3$  kcal./mole; higher values of  $n$  are not wholly excluded. A tentative formula for the complex is



and its formation explains many of the results of earlier workers.

#### EXPERIMENTAL.

*Preparation of the Solutions of Methylmagnesium Iodide.*—Previously described methods (Mackle and Ubbelohde, *loc. cit.*) were used for the preparation of ethereal solutions of methylmagnesium iodide from specially pure magnesium, carefully purified ether, and methyl iodide. Dry oxygen-free nitrogen was used to protect the ethereal solutions at every stage during preparation, transfer, and storage of all the solutions. An improved form of vessel was devised for the preparations (Fig. 1), since it had been found that atmospheric moisture depositing on the outside of the condenser tended to seep into the flask unless the appropriate ground joint was reversed as in Fig. 1. As the last stage of the drying process, purified ether was in all cases distilled in nitrogen from a Grignard reaction, immediately before use (Mackle, *Proc. Irish Acad.*, in the press).

*Preparation of Solutions of Magnesium Iodide.*—The same apparatus was used as above. Pure resublimed iodine (May and Baker) (30 g.), dissolved in purified ether, was added very gradually from the dropping funnel to the reaction flask containing 5 g. of magnesium and enough ether to cover it. The reaction was violent at first, and was completed to disappearance of the iodine colour by heating under reflux. The resulting mixture (present as two layers) was siphoned off and kept in darkness under nitrogen till required. If the magnesium iodide crystallised out on storage, it was brought into solution by gently warming the outside of the vessel with a swab wetted with hot water.

*Photochemical Decomposition of Magnesium Iodide in Ether.*—Menschutkin reported (*Z. anorg. Chem.*, 1906, **49**, 34) that magnesium iodide dietherate became yellowish-brown after several hours and brown after a day. Similar behaviour was observed in the present experiments in spite of the rigorous precautions against atmospheric oxidation. Special tests showed that the oxygen-free solutions of magnesium iodide become brown and cloudy on exposure to daylight, or to the light from a mercury arc, but that solutions kept in the dark remained clear and colourless indefinitely. All work with the solution was therefore carried out in darkness or in diffuse light.

*The Solubility Curve of Magnesium Iodide Dietherate in Ether.*—In view of the uncertainty attaching to Menschutkin's observations (*loc. cit.*), owing to possible photochemical decomposition, the solubility curve of magnesium iodide dietherate was redetermined between 0° and 20°. The two-phase region from 23° to 38°, also investigated by Menschutkin, was not suitable for the present purpose. By use of the apparatus shown in Fig. 2 the magnesium iodide solution, prepared as described, was transferred to the Pyrex vessel (A), using a counter-current of nitrogen. The vacuum vessel (V) was then filled with ice, and the magnesium iodide dietherate caused to crystallise, leaving an ether solution with traces of

magnesium hydroxide in suspension. This was withdrawn and replaced by pure ether. The whole apparatus was kept in darkness.

For solubility determinations the vessel (*A*) was heated, with shaking, a few degrees above the temperature of the water in the vacuum-flask. This led to dissolution of part of the crystals. It was then immersed in (*V*) and shaken occasionally until its temperature dropped to that of the water in the flask (*V*). The calcium chloride-soda lime tube (*C*) was then closed. Dry oxygen-free nitrogen which flowed continuously in by (*D*) and out by (*C*) built up a pressure and forced over the clear saturated solution along tube (*B*). Six portions of this solution were collected in six dried and weighed conical flasks (provided with stoppers). The stoppers were replaced immediately and the conical flasks plus contents were reweighed.

FIG. 1.  
*Apparatus for making up solutions.*

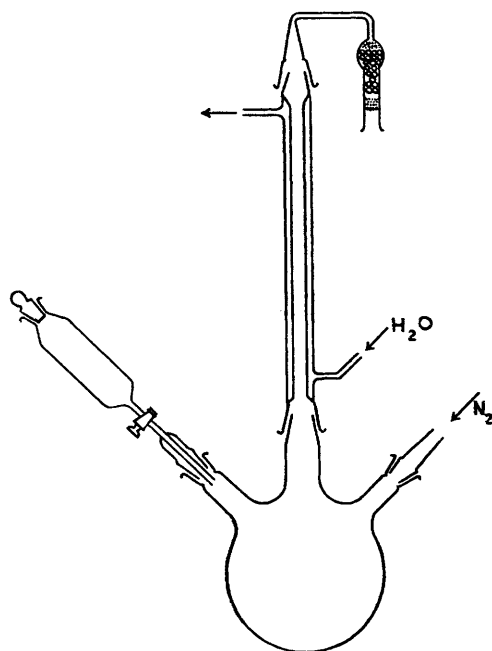
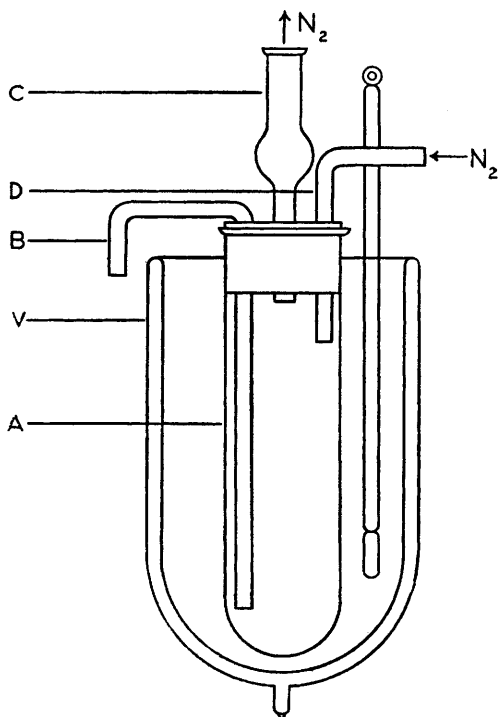


FIG. 2.  
*Determination of solubility of  $\text{MgI}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ .*



The iodide content of three of these was determined by the standard Volhard method. The other three were used for determination of the magnesium content by 8-hydroxyquinoline. This process was repeated for a range of temperatures from  $0^\circ$  to  $20^\circ$ . Although it was not strictly necessary to determine both the iodide and magnesium contents to calculate the solubility, both determinations were made so as to test the purity of the magnesium iodide. The ratio in the most unfavourable case was 1 : 1.93 and the average 1 : 1.98. Data obtained for the solubility at different temperatures are given in Table I. The values now obtained agree well with Menshutkin's data (cf. Fig. 3).

TABLE I.

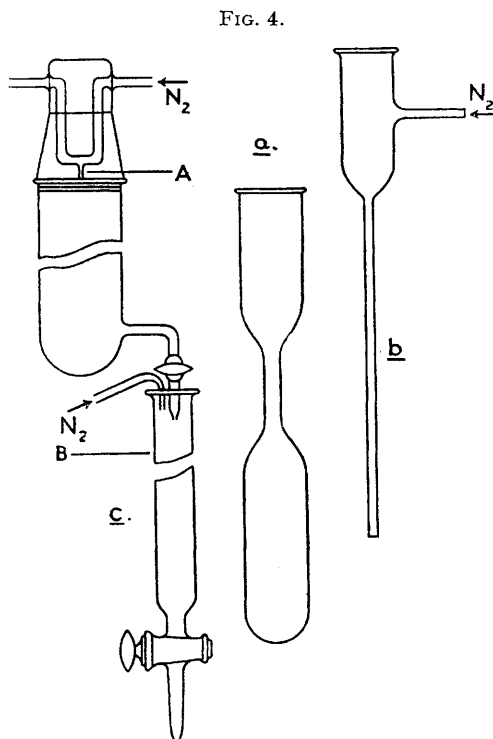
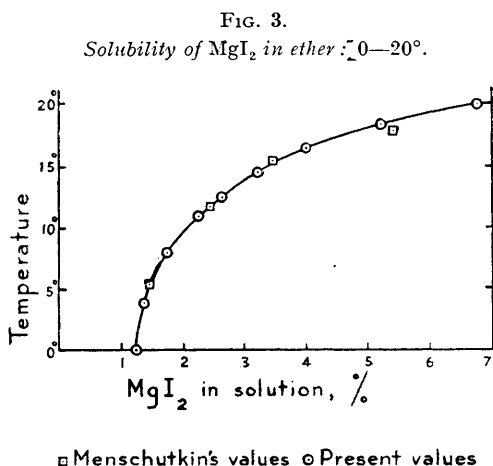
*Solubility of magnesium iodide dietherate.*

Temp.....	$0.0^\circ$	$4.0^\circ$	$8.0^\circ$	$11.0^\circ$	$12.6^\circ$	$14.4^\circ$	$16.6^\circ$	$18.5^\circ$	$20.0^\circ$
Mass-% $\text{MgI}_2$ in solution .....	1.21	1.35	1.75	2.25	2.58	3.22	4.02	5.23	6.78

*Systems Used to Study the Equilibrium,  $\text{CH}_3\text{MgI}-\text{MgI}_2-(\text{C}_2\text{H}_5)_2\text{O}$ .*—Different volumes of methylmagnesium iodide and magnesium iodide solution of known strength were mixed in glass tubes, and the tubes were sealed under nitrogen. They were kept in darkness at constant temperature, and their compositions were determined by a freezing-point method.

The solutions of methylmagnesium iodide and magnesium iodide, prepared as described, were transferred in an atmosphere of nitrogen to two separate containers. One of these, fitted with a cap and a tap in the side arm, is shown at the top left of Fig. 4. A small flow of protective nitrogen issued from the capillary opening (*A*). The burette (*B*) was set up so that the end of the side-arm of the container rested inside the top of the burette, and all air was excluded by a flow of dry oxygen-free nitrogen as shown.

The two burettes were respectively filled with the two solutions from the containers, and measured volumes of each were added to a number of Pyrex vessels (Fig. 4a) by means of the filling funnel (Fig. 4b). This was fitted with a side-arm for a nitrogen lead to give an inert atmosphere around the tip of the burette. The long stem of the funnel served to avoid any wetting of the constriction in the vessel by the solutions, which was important to obtain a good seal at a later stage.



After filling, each Pyrex vessel was cooled in solid carbon dioxide-methylated spirit to *ca.*  $-80^\circ$ . The filling funnel was then withdrawn, and the tube quickly sealed at the top of the constriction using a coal gas-oxygen flame.

The compositions of the two stock solutions were determined by evaluating, in known volumes of each, the amount of Grignard reagent and of magnesium iodide as previously described. Good agreement was obtained between determinations at the beginning and end of a series of filling operations, showing that the difficulties in handling these solutions had been successfully overcome. The mass of 10 ml. of each solution was also determined (see below).

TABLE II.

Original composition of contents of sealed tubes.

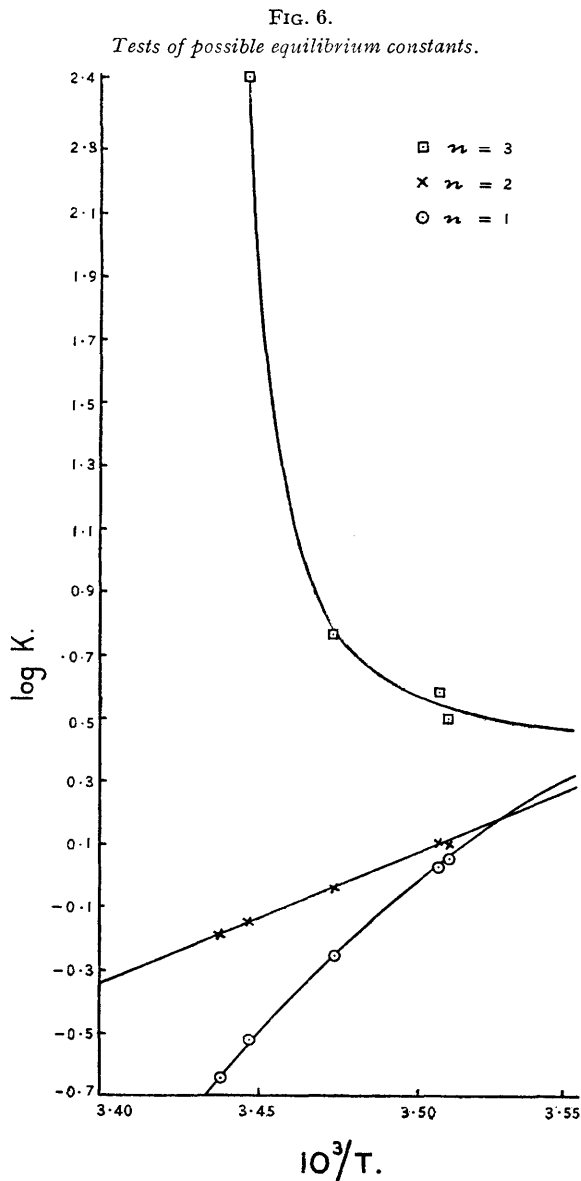
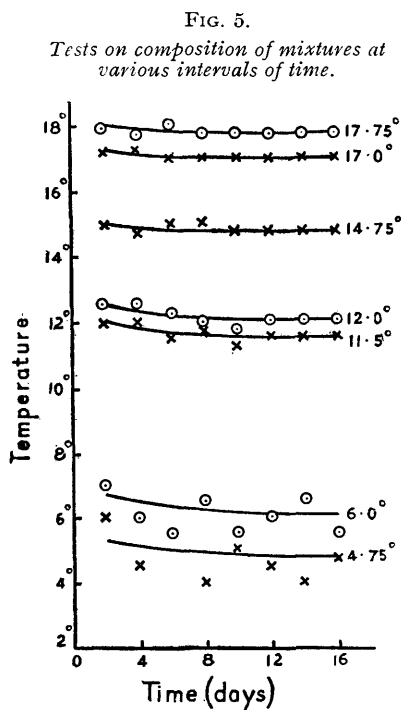
No. of tube.	Moles of ether $\times 10^2$ .	Moles of $MgI_2$ $\times 10^4$ .	Moles of $CH_3MgI$ $\times 10^4$ .	No. of tube.	Moles of ether $\times 10^2$ .	Moles of $MgI_2$ $\times 10^4$ .	Moles of $CH_3MgI$ $\times 10^4$ .
1 (a)	19.2	45.7	89.2	6 (b)	15.3	48.6	41.0
2 (b)	18.4	45.7	82.0	8 (b)	14.9	51.2	32.3
4 (b)	16.7	47.7	54.8	9 (a)	15.6	55.4	30.8
5 (a)	15.8	46.8	49.5				

Vessels marked (a) were stored in the dark at  $20^\circ$  and those marked (b) in the dark at  $0^\circ$ . The contents were tested from time to time as described in the following paragraphs.

*Determinations of Composition as a Function of Time.*—To find whether the contents of the sealed vessels changed in composition with time, as would be the case if a Schlenk equilibrium were slowly reached, a method of analysis depending on the solubility of the magnesium iodide was used. This consisted in cooling the sealed vessels until the excess of magnesium iodide started to crystallise, and then warming them very slowly (*ca.*  $1^\circ$  in every 2 minutes) with continuous shaking, until dissolution was just complete. At this temperature the contents of the vessel formed a saturated solution of magnesium iodide. On the assumption that the presence of organo-metallic compounds did not affect the thermodynamic activity of the magnesium iodide (as is probably approximately true for the concentrations used), the molar fraction in solution could be obtained from the observed solution temperature. By plotting this solution temperature as a function of the time of storage, it was possible to obtain direct information as to whether slow shifts of equilibrium were taking place over a period of days.

Such plots are recorded in Fig. 5. The results are more erratic at the low temperatures on account of the shape of the solubility curve (Fig. 3), but the main conclusion is that no slow shift of equilibrium was observed, involving a change in the molar fraction of magnesium iodide.

To test this conclusion more searchingly, the storage temperatures of vessels (a) and (b) of Table II were reversed after 14 days. No change in the solution temperature for any vessel was observed over a further 6 days, showing that the storage temperature did not affect the position of equilibrium as determined from the freezing point of magnesium iodide dietherate. All the results are included in Table III, but, because of the less reliable data at the lower temperatures, results for these have not been plotted in Figs. 6 and 7.



Calculation of the Composition of the Solutions in the Sealed Vessels.—This may be illustrated by a typical example.

Results. Initial determinations:

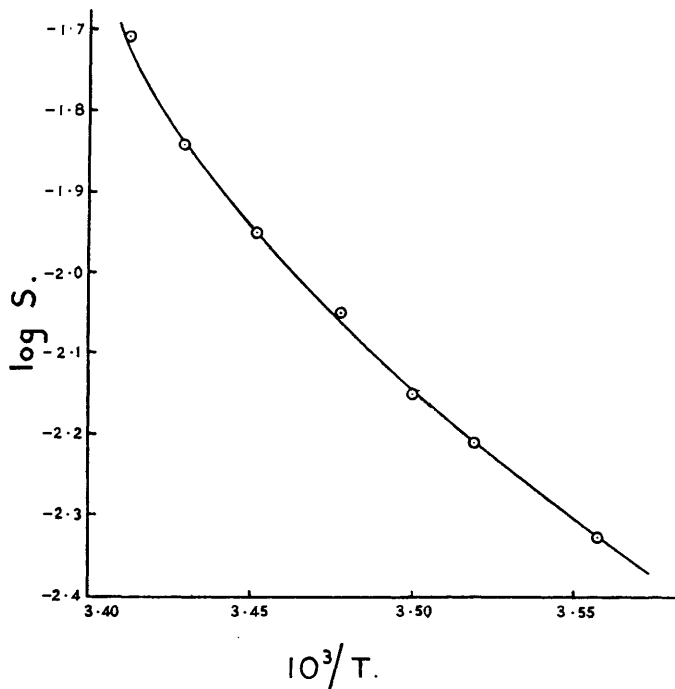
Strength of $\text{CH}_3\text{MgI}$ solution	= 1.36 g. per 10 ml. of solution.
Mass of $\text{CH}_3\text{MgI}$ solution	= 8.215 g. per 10 ml. of solution.
Strength of $\text{MgI}_2$ solution	= 14.6 g. per 100 g. of solution.
Mass of $\text{MgI}_2$ solution	= 8.030 g. per 10 ml. of solution.

By use of these data, full details of the initial solutions in the tubes can be calculated. For example, from Fig. 3 a temperature of 287.8° K. corresponds with 3.22 g. of magnesium iodide per 100 g. of solution, *i.e.*, a molar fraction of 0.401. If the same molar fraction is assumed to apply for the same freezing point in the mixture (*i.e.*, Raoult's law), the results in Table III could be calculated.

At the end of the experiments several of the tubes were opened under nitrogen and were slightly cooled to induce partial crystallisation. The supernatant solution was sucked off and removed by washing with ether. Analysis of the residual crystals showed they were pure magnesium iodide dietherate. This verified the conclusion that no organo-metallic compound crystallised with the magnesium iodide under the conditions of the experiments, showing that the correct solubility curve was used.

FIG. 7.

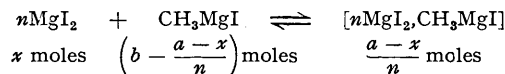
Logarithmic solubility curve of  $\text{MgI}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ .



## DISCUSSION.

*Formation of Complexes in Solution.*—The results of the preceding section provide no evidence of a slow equilibrium of the type of equation (1) or (2). Furthermore, comparison of columns 1 and 2 of Table III shows that a large proportion of "free" magnesium iodide disappears from solution, the amount disappearing increasing with the amount of methylmagnesium iodide originally present. This confirms the general observations on chlorides by other authors (Doering and Noller, *loc. cit.*). Some kind of complex formation appears to be indicated.

In order to give a more precise explanation of the data now obtained, we may examine tentative equilibria of the general type



where  $a$  is the no. of moles of magnesium iodide initially,  $b$  is the no. of moles of methylmagnesium iodide, and  $x$  is the no. of moles of magnesium iodide at equilibrium. Search must then be made for an equilibrium constant :

$$K = [n\text{MgI}_2, \text{CH}_3\text{MgI}] / [\text{CH}_3\text{MgI}][\text{MgI}_2]^n \quad \dots \quad (3)$$

From the data in Table II and from the solubility curve of magnesium iodide dietherate, the various concentrations are readily calculated for values of  $n = 1, 2, 3$ , etc., and the corresponding equilibrium constants may be computed as shown in Table III. It is assumed that no extensive

dissociation of magnesium iodide or of methylmagnesium iodide into ions occurs in ether solution, and that the complex is not extensively dissociated into ions.

TABLE III.  
Equilibrium data.

$a \times 10^4$ initial MgI <sub>2</sub> , moles.	$x \times 10^4$ equilib. MgI <sub>2</sub> , moles.	$b \times 10^4$ initial CH <sub>3</sub> MgI, moles.	$v \times 10^3$ litres.	$K$ $n = 1.$	$K$ $n = 2.$	$K$ $n = 3.$	Temp. ( $T$ ) °K.	$10^3/T.$
45.7	7.9	89.2	20.9	1.94	1.88	3.05	277.8	3.599
45.7	8.2	82.0	19.85	2.10	1.74	2.60	279.1	3.583
46.8	11.2	49.5	16.9	3.86	1.28	1.06	285.1	3.507
47.7	11.3	54.8	17.9	3.14	1.25	1.13	284.6	3.510
48.6	14.5	41.0	16.4	5.85	0.91	0.56	287.8	3.474
51.2	18.8	32.3	15.9	274	0.72	0.30	290.1	3.447
55.4	22.2	30.8	16.5	—	0.65	0.23	290.8	3.438

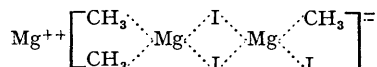
It must be kept in mind that present evidence indicates that the equilibrium (3) is rapidly established, so that the value of  $K$  corresponds in each experiment to the freezing point at which it is evaluated. To test equation (3) it is therefore necessary to use the integrated form of the van't Hoff isochore

$$\log K_1 - \log K_2 = (-\Delta H/4.57)(1/T_1 - 1/T_2)$$

Plots of  $\log K$  against  $1/T$  (Fig. 6) give no evidence of a mass action constant for  $n = 1$ . Data for  $n = 2$  give a good straight line, but  $n = 3$  is not wholly excluded.

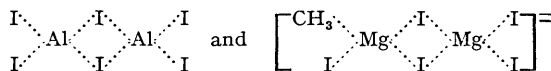
In the plots, allowance has been made for the fact that solution temperatures were measured just as the last few particles of magnesium iodide dietherate were disappearing. These amounts were estimated to be not more than 0.02 g., from which error limits in the slopes of the plots of  $\log K$  against  $1/T$  could be determined.  $\Delta H$  in equation (3) is  $-18.3 \pm 1.1$  kcal. if  $n = 2$ , or  $41.1 \pm 1.5$  kcal. if  $n = 3$ .

*Comparison with Other Lines of Evidence on the Formation of Complexes.*—(a) Molecular-weight determinations from the elevation of boiling point of dimethyl ether by methylmagnesium iodide indicate molecular weights rather greater than  $2\text{CH}_3\text{MgI}$  (Terentjew *Z. anorg. Chem.*, 1926, 156, 73). Evidence of association has also been recorded by Meisenheimer and Schlichenmaier (*Ber.*, 1928, 61, 721). In both sets of experiments the solutions were not free from criticism, showing opalescence and a Mg : I ratio considerably below 1 : 2. However, the results are in general agreement with the present findings, indicating complexes which may tentatively be written as



(b) Conductance experiments are in general agreement with the formation of complex anions containing magnesium. Evans, Braithwaite, and Field (*loc. cit.*) propose the equilibrium,  $\text{R}_2\text{Mg}_2\text{X}_2 \rightleftharpoons [\text{RMgX}_2]^- + [\text{MgR}]^+$ , but the complex suggested by the present findings does not appear to be contradicted by the experiments on electrolysis of organo-magnesium halides.

(c) The magnitude of the heat of complex formation,  $-18.3 \pm 1.1$  kcal., may be compared with the value ( $-22.5$ ) for the equilibrium (Fischer and Rahifs, *Z. anorg. Chem.*, 1932, 205, 1),  $2\text{AlI}_3 \rightleftharpoons \text{Al}_2\text{I}_6$ . It is suggested that the bonds in the resonance systems



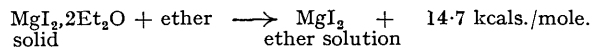
are closely similar in electronic behaviour. This would require the  $\text{CH}_3\text{-Mg}$  bond to have about the same ionic character as the  $\text{I-Mg}$  bond in methylmagnesium iodide. Some support for this is provided by the almost instantaneous exchange reactions in diethyl ether, of the type  $\text{ZnCl}_2 + \text{C}_2\text{H}_5\text{MgBr} \rightleftharpoons \text{Zn}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{MgBrCl}$  (Evasn and Pearson, *J. Amer. Chem. Soc.*, 1942, 64, 2868).

These very rapid reactions suggest that the aliphatic Grignard compounds are perhaps best compared with ion-pair systems  $\bar{\text{R}}\text{Mg}\bar{\text{X}}$ . In the case of aromatic Grignard compounds the complex anion appears to grow to the size of a colloidal micelle (Evans and Pearson, *loc. cit.*) by association. This may be tentatively attributed to the high polarisability of the aromatic nucleus leading to the continuation of association to values of  $n \gg 2$ .

In view of present findings it may be expected that, when a Grignard reagent can react in

alternative ways, the extent to which the alternative reactions occur should be modified by adding excess of magnesium iodide so as to shift the extent to which complex formation occurs. Some evidence of this has previously been published by Mackle and Ubbelohde (*loc. cit.*).

*Heat of Solution of Magnesium Iodide Dietherate in Diethyl Ether.*—From the data recorded in Table I, and from those of Menshutkin, we may calculate the heat of solution for the process



using the equation  $\text{dln}S/\text{d}T = \Delta H/RT^2$ , where the solubility  $S$  is expressed as a molar fraction of magnesium iodide dietherate.

The slope of  $\log S$  plotted against  $1/T$  gives a shallow curve (Fig. 7). The average slope corresponds with  $\Delta H = 14.7$  kcal./mole.

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