# 549. *The Gattermann–Koch Reaction. Part I. Thermodynamics.*

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Calculation of $\Delta G°$ for $C_6H_6 + CO \longrightarrow C_6H_5{\cdot}CHO$ shows that the reaction probably does not proceed in the absence of complex formation between catalytic halide and product. Two kinds of calorimetric experiment have been made : (I) catalytic halide plus excess of benzaldehyde leads to $Q$, the heat of complex formation; (II) catalytic halide plus equivalent amounts of benzaldehyde leads to the molecularity of the complex and a value of $K$, the dissociation constant of the complex, and hence to $\Delta G°$ for the formation of the complex. Values of $-\Delta G°$ for complex formation are sufficiently large to make the equilibrium in the Gattermann–Koch reaction favourable. Bond energies for the complex are calculated on the basis of certain simplifying assumptions.

The Gattermann–Koch reaction is fundamentally a reaction in which the CO group is introduced into aromatic molecules under the influence of a molecular proportion of a Friedel–Crafts catalyst, usually aluminium chloride or bromide. In their original paper Gattermann and Koch (*Ber.*, 1897, **30**, 1622) passed a 2CO : 1HCl mixture through 30 g. of toluene and 45 g. of aluminium chloride, a necessary further addition being 4 g. of cuprous chloride. *p*-Tolualdehyde was obtained in 50% yield at 20—25°. The synthesis failed with benzene but, when aluminium bromide was used, a 90% yield of benzaldehyde was obtained (Reformatski, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 154; Gattermann, *Annalen*, 1906, **347**, 347). The synthesis has been developed in a number of ways. For instance, an 85% yield of benzaldehyde may be obtained with aluminium chloride if the carbon monoxide is used at 40—90 atm. pressure (D.R.-P. 281,212; B.P. 3152). Here hydrogen chloride and cuprous chloride were dispensed with, although the inevitable presence of traces of moisture would have given rise to some hydrogen chloride. A high-pressure synthesis of this kind has been tried, using titanic chloride as a promoter in place of cuprous chloride (B.P. 334,009; U.S.P. 1,939,005), and another using benzaldehyde and aluminium chloride complex as a promoter (U.S.P. 1,989,700).

In a further patent (D.R.-P. 403,489) a process is described in which benzaldehyde is synthesised, aluminium chloride and carbon monoxide being used at atmospheric pressure. No cuprous chloride was used, but a proportion of nitrobenzene was added to bring the aluminium chloride into solution. A 90% yield was claimed, but we have failed to confirm this result. The aluminium chloride–benzaldehyde complex has been found to be a catalyst for the benzaldehyde synthesis (*Tech. Krupp*, 1938, **6**, 59) and has been used by Holloway and Krase (*Ind. Eng. Chem.*, 1933, **25**, 497) to reduce the induction period in the high-pressure synthesis of benzaldehyde with aluminium chloride. Holloway and Krase (*loc. cit.*) find that water may replace hydrogen chloride in the high-pressure synthesis, and that there is an optimum temperature for the reaction of 20°. Hardy (*J. Soc. Chem. Ind.*, 1948, **67**, 150) finds the optimum temperature to be 35° for the high-pressure synthesis of benzaldehyde with aluminium chloride. He finds that the aluminium chloride complexes with either benzaldehyde or ethyl ether function as accelerators. Calculations by Campbell and Eley (*Nature*, 1944, **154**, 85) have shown that the synthesis of benzaldehyde is only rendered thermodynamically favourable by the formation of benzaldehyde–aluminium chloride complex as a stable end-product. This result explained a failure to find a true contact synthesis of benzaldehyde when working at 1 atm. pressure (Eley, Ph.D. Thesis, Cambridge, 1940).

The Gattermann–Koch reaction forms a suitable system in which to study the fundamental action of Friedel–Crafts catalysts, and the results referred to above pose a number of interesting problems. We have, therefore, in the first place revised the calculations of Eley and Campbell (which were never published in full), and made a careful calorimetric study of the complexes between benzaldehyde and a series of Friedel–Crafts catalysts. The results of this work form a basis upon which we may later discuss the kinetics of the reaction and the mode of action of the catalysts.

*Thermodynamic Calculations.*—We first discuss the overall reaction $C_6H_6(l) + CO(g) \longrightarrow C_6H_5{\cdot}CHO(l)$. Table I gives the data used in the calculation (all data are at 1 atm. pressure).

TABLE I.

| Substance. | Heat of combustion, kcals./mole; 298° K. | Entropy, cal./deg./mole; 298° K. | Heat capacity, cal./deg./mole; 298° K. |
|---|---|---|---|
| Benzene (l.) | 781·0 (R) | 41·5 (P) | 31·9 (I.C.T.) |
| CO (g.) | 67·6 (R′) | 47·3 (R′) | 7·0 (I.C.T.) |
| Benzaldehyde (l.) | 841·3 (K) | 57·4 (E) | 45·4 (I.C.T.) |

R, Rossini *et al.*, *Bur. Stand. J. Res.*, 1945, **34**, 65.
P, Pitzer and Rossini, *ibid.*, 1946, **37**, 95.
I.C.T., International Critical Tables.
R′, Rossini, *Bur. Stand. J. Res.*, 1939, **22**, 407.
K, Kharasch, *ibid.*, 1929, **2**, 359 (at 293° K.)
E, Estimated from data in Parks and Huffmann, "Free Energies of Some Organic Compounds," New York, 1932.

From these data we have

$$\Delta H^{\circ}_{298} = -7300 \text{ cals.}; \quad \Delta S_{298} = -31{\cdot}4 \text{ cals./deg./mole}; \quad \Delta C_{p298} = 6{\cdot}5 \text{ cals./deg./mole.}$$

We can then calculate $\Delta G^{\circ}$ and the equilibrium constant $K$ by the equation

$$-\boldsymbol{R}T \ln K = \Delta G^{\circ} = \Delta H^{\circ}_{298} - T.\Delta S^{\circ}_{298} + \Delta C_p(T - 298) - T\Delta C_p \ln T/298 \quad . \quad . \quad (1)$$

The results are given in Table II. These positive values of $\Delta G^{\circ}$ and the derived $K$ lead to a benzaldehyde yield at toom temperature of about 2% (calculated on the benzene), decreasing at increasing temperature. The calculated value of $K$ is very sensitive to small changes in $\Delta H$ and the chief error in the above calculations lies in the uncertainty in the thermodynamic data for benzaldehyde. It seems clear that the reaction as written above is thermodynamically unfavourable, or at best only just favourable. The next step is to consider the overall reaction

TABLE II.

*Benzaldehyde equilibria.*

| $T^{\circ}$, K. | 298 | 323 | 373 |
|---|---|---|---|
| $\Delta G^{\circ}$ | 2,060 | 2,830 | 4,350 |
| $K \times 10^3$ | 31·6 | 12·6 | 2·9 |

$$C_6H_6(l) + CO(g) \longrightarrow C_6H_5{\cdot}CHO(l)\,; \ \Delta G_1^{\circ}$$

$$C_6H_5{\cdot}CHO(l) + \tfrac{1}{2}Al_2Cl_6(s) \longrightarrow C_6H_5{\cdot}CHO,AlCl_3(s)\,; \ \Delta G_2^{\circ}$$

To understand the excellent yields obtainable in the Gattermann–Koch reaction, it is necessary to obtain an estimate of $\Delta G_2^\circ$. This we have done in the first place by a measurement of the heat of mixing of benzaldehyde, not only with aluminium chloride, but with the bromide and a whole range of related halides, from which $\Delta H$ is obtained.

We have also applied in a few cases a new but somewhat laborious analysis of calorimetric data leading to an estimate of $\Delta G$. Although logically it would be best to describe this analysis first, we shall, in fact, describe the measurements of $\Delta H$ first, on account of their simplicity.

## EXPERIMENTAL.

Details of the techniques used will appear in a forthcoming paper, and we give only a brief description here. The method was to place a weighed amount of purified aluminium chloride under 60 c.c. of dried chlorobenzene in the calorimeter, an unsilvered Dewar vessel provided with a cap carrying a stirrer, a " Thermistor " (for temperature measurement), an electrical heater (for determination of the water equivalent), and the lead-in tube for the delivery coil, containing the benzaldehyde at 25°. The whole apparatus was immersed in a thermostat at 25°. At zero time the benzaldehyde was blown over into the calorimetric liquid by a current of dry air, and the temperature–time curve followed. Complex formation and heat evolution were usually complete in 0·5—4 minutes, and the water equivalent of the calorimeter and contents was then measured.

All heats quoted are per mole of halide calculated as the monomer (for example, 133·3 g. for aluminium chloride).

The exact amount of benzaldehyde delivered into the calorimeter from the delivery coil is, in general, unimportant, compared with the accuracy with which the weight of salt is known, but the coils were calibrated as follows :

5-c.c. coil : 4·311, 4·265, 4·296, 4·178, 4·259 g. Mean = 4·26 g. = 0·0402 mole.
1-c.c. coil : 0·7930, 0·8270, 0·7730, 0·8129, 0·8045, 0·8047, 0·8157. Mean = 0·8044 g. = 0·0076 mole.

The total error in the calorimetric measurements was estimated as perhaps 1% and confirmed by measurements of heats of neutralisation.

*Materials.—Chlorobenzene.* The I.C.I. product was washed with 50% sulphuric acid and water, dried ($CaCl_2$), and fractionated through a column (seven theoretical plates); b. p. 131·2—132·7°; $n_D^{20}$ 1·5245 (1·5248).

*Benzaldehyde.* The B.D.H. product was dried ($CaCl_2$) and distilled in a stream of nitrogen; b. p. 178°; $n_D^{17\cdot5}$ 1·5460 (1·5463).

*Bromobenzene.* The B.D.H. product was dried ($CaCl_2$) and fractionated; b. p. 156°; $n_D^{25}$ 1·5565 ($n_D^{20}$ 1·5598).

*Carbon tetrachloride.* The I.C.I. product was dried ($CaCl_2$) and fractionated; b. p. 77·0°.

(Values of $n^t_D$ in parentheses are from I.C.T. or other tables.)

*Aluminium chloride.* A mixture of equal parts of B.D.H. aluminium chloride and aluminium powder was sublimed in a stream of dry hydrogen chloride. The product was a white crystalline solid free from ferric chloride. Before use it was powdered. In certain cases (specified) it was further sublimed in dry nitrogen to remove adsorbed hydrogen chloride.

*Aluminium bromide.* The B.D.H. product was recrystallised from carbon disulphide, all traces of which were removed by pumping in a vacuum desiccator. The product was a dirty-white powder which darkened on keeping.

*Aluminium iodide.* This was prepared by the method of Palmer and Elliot (*J. Amer. Chem. Soc.*, 1938, **60**, 1852). Iodine was heated at 300° with excess of aluminium in an evacuated tube until all traces of free iodine had disappeared. By distillation in a vacuum a white solid was obtained which liberated iodine when stored.

*Ferric chloride.* B.D.H. " AnalaR."

*Titanic chloride, stannic chloride, antimony pentachloride, and antimony trichloride.* From freshly opened B.D.H. bottles.

*Zirconium tetrachloride.* The F. A. Hughes product, stated to contain 2% of ferric chloride, was used.

*Boron trifluoride–ether.* This was obtained from the General Chemical Company, New York; b. p. 126° (Found : B, 7·6—7·8. Calc. for $BF_3,C_4H_{10}O$ : B, 7·7%).

*Beryllium chloride.* Merck's anhydrous.

*Cuprous chloride.* This was obtained as a white powder by reduction of the cupric salt with sulphur dioxide.

*Stannous chloride (anhydrous).* This was prepared by dehydrating the hydrate with acetic anhydride.

*Sodium aluminium chloride.* By fusing exactly equimolecular quantities of sodium chloride and aluminium chloride in an atmosphere of dry nitrogen (Norris and Klemka, *J. Amer. Chem. Soc.*, 1940, **62**, 1432), this was obtained as a dirty white powder, m. p. 150°.

Calcium chloride, mercuric chloride, zinc chloride, cupric chloride, ferrous chloride, ferric chloride (hydrated), and stannous chloride (hydrated) were all B.D.H. products.

The calorimetric liquids were stored over calcium chloride, and the halides in desiccators. Calcium chloride tended to promote oxidation of benzaldehyde to benzoic acid, and so was not used in this case. A fresh sample was distilled before each set of runs and stored in a dark bottle. Incidentally, benzoic acid gives no heat of mixing with aluminium chloride.

*Results.*—If we consider the reaction Halide + $nC_6H_5\cdot CHO \rightleftharpoons$ Halide,$(C_6H_5\cdot CHO)_n$ in the first group of experiments, we measure the heat of this reaction at 25° by working with a large molecular excess of benzaldehyde, using the 5-c.c. delivery coil. On the average, our conditions in this first series of experiments correspond to the range 0·001—0·006 mole of halide and 0·04 mole of benzaldehyde. These conditions, together with the large heats actually observed in most cases, suggest that the reaction is essentially irreversible and that complex formation is virtually complete.

In the second group of experiments we work with a range 0·001—0·02 mole of halide and 0·0076 mole of benzaldehyde as delivered by the 1-c.c. coil. By working in this "equivalence zone" we can gain information about $n$ in the above equation and also the equilibrium constant $K$ for complex formation. The literature in general points to $n = 1$, except in the cases of stannic, titanic, and zirconium chloride, where $n = 2$. Our second group of experiments confirm these values of $n$ in the cases examined, but the laborious nature of the work has precluded a detailed examination of all cases.

*Group I.*—The general procedure was to measure the heat evolved on addition of 4·26 g. of benzaldehyde to various weights $w$ of metallic halide, of molecular weight (as monomer) $M$. If $S$ is the heat of solution of benzaldehyde in the calorimetric liquid, usually chlorobenzene, we find $x = S + wQ/M$.

A plot of $x$, the heat evolved, against $w$ then allows us to calculate $Q$ (the heat of complex formation) from the slope of the resultant straight line. In the case where the complex is either insoluble or completely soluble in the chlorobenzene, $Q$ refers to a clearly defined final state, but in some cases partial solubility is found. Heat effects arising from the solubility of the complex may safely be assumed to be small. The analysis of $Q$ into contributory terms is carried out later.

We shall expect the intercept $S$ to be the same for the same benzaldehyde–calorimetric liquid combination. For substances like titanic chloride, which are almost impossible to transfer without a small amount of hydrolysis, the intercept $S$ may be markedly larger than the heat of solution. Since $Q$ is obtained from the slope, however, it will be unaffected by hydrolysis of the salt, provided that this is relatively small and random over the series.

The results are collected in Table III, and the graphs from which the $Q$ values are calculated are shown in Figs. 1*a*, *b*, *c*. It will be convenient to discuss each halide separately.

TABLE III.

*Heats of complex formation, with 4·26 g. of benzaldehyde.*

| Run. | Wt. of halide (g.). | Heat (cals.). | Run. | Wt. of halide (g.). | Heat (cals.). | Run. | Wt. of halide (g.). | Heat (cals.). |
|---|---|---|---|---|---|---|---|---|
| | $AlCl_3$. | | | $AlI_3$. | | | $TiCl_4$. | |
| 154 | 0·296 | 49·5 | 332 | 0·604 | 70·4 | 129 | 0·977 | 152·4 |
| 155 | 0·538 | 95·5 | 333 | 1·127 | 124·1 | 130 | 0·597 | 79·3 |
| 156 | 0·814 | 144·1 | 334 | 0·725 | 82·0 | 131 | 0·765 | 110·4 |
| 157 | 0·221 | 31·9 | 335 | 0·887 | 97·4 | 132 | 0·503 | 63·8 |
| 158 | 0·744 | 134·2 | | | | 133 | 0·959 | 149·5 |
| 159 | 0·412 | 76·0 | | $FeCl_3$. | | | | |
| 160 | 0·255 | 43·8 | 107 | 0·649 | 49·5 | | $SbCl_5$. | |
| | | | 109 | 0·917 | 69·5 | 115 | 1·786 | 104·8 |
| | $NaAlCl_4$. | | 110 | 0·293 | 21·1 | 116 | 1·010 | 37·1 |
| 151 | 0·449 | 36·1 | 111 | 0·512 | 37·1 | 118 | 0·588 | 11·8 |
| 152 | 0·865 | 60·7 | 168 | 0·315 | 21·7 | 121 | 1·125 | 49·8 |
| 153 | 0·669 | 43·4 | | | | 122 | 1·238 | 56·5 |
| | | | | $SnCl_4$. | | | | |
| | $AlBr_3$. | | 123 | 1·030 | 101·3 | | $ZrCl_4$. | |
| 134 | 0·425 | 44·0 | 124 | 1·517 | 151·9 | 144 | 0·521 | 34·4 |
| 135 | 0·607 | 65·9 | 125 | 0·608 | 54·3 | 145 | 0·921 | 71·6 |
| 136 | 1·290 | 165·1 | 126 | 0·992 | 98·4 | 146 | 0·695 | 50·6 |
| 137 | 0·983 | 121·8 | 127 | 0·485 | 39·8 | 147 | 0·808 | 56·4 |
| 140 | 0·722 | 93·2 | 128 | 0·566 | 49·4 | 148 | 0·276 | 20·0 |
| 141 | 0·343 | 38·3 | | | | 149 | 1·182 | 91·7 |
| 142 | 0·569 | 69·5 | | $SbCl_3$. | | | | |
| 143 | 1·079 | 134·5 | 112 | 0·580 | 5·3 | | | |
| | | | 113 | 1·405 | 19·4 | | | |
| | | | 114 | 0·979 | 12·1 | | | |

*Aluminium chloride.* Chlorobenzene was used as calorimetric liquid. Runs 154—157 were carried out, using aluminium chloride sublimed in hydrogen chloride, and runs 158—160 using aluminium chloride sublimed in nitrogen. Both sets of results lie on the same straight line in Fig. 1*a*. The end-product in all cases was a colourless solution from which the complex appeared to be partly precipitated as a white solid; a trace of hydrogen chloride was evolved in some cases.

$Q$ = 24·7 kcals. per mole of $AlCl_3$.
$S$ = − 5 cals. (4·26 g. of benzaldehyde in 60 c.c. of chlorobenzene).

Since aluminium chloride is insoluble in chlorobenzene and there is evidence that the complex is 1 : 1 (see next section), we consider that the heat evolved, $Q$, corresponds essentially to

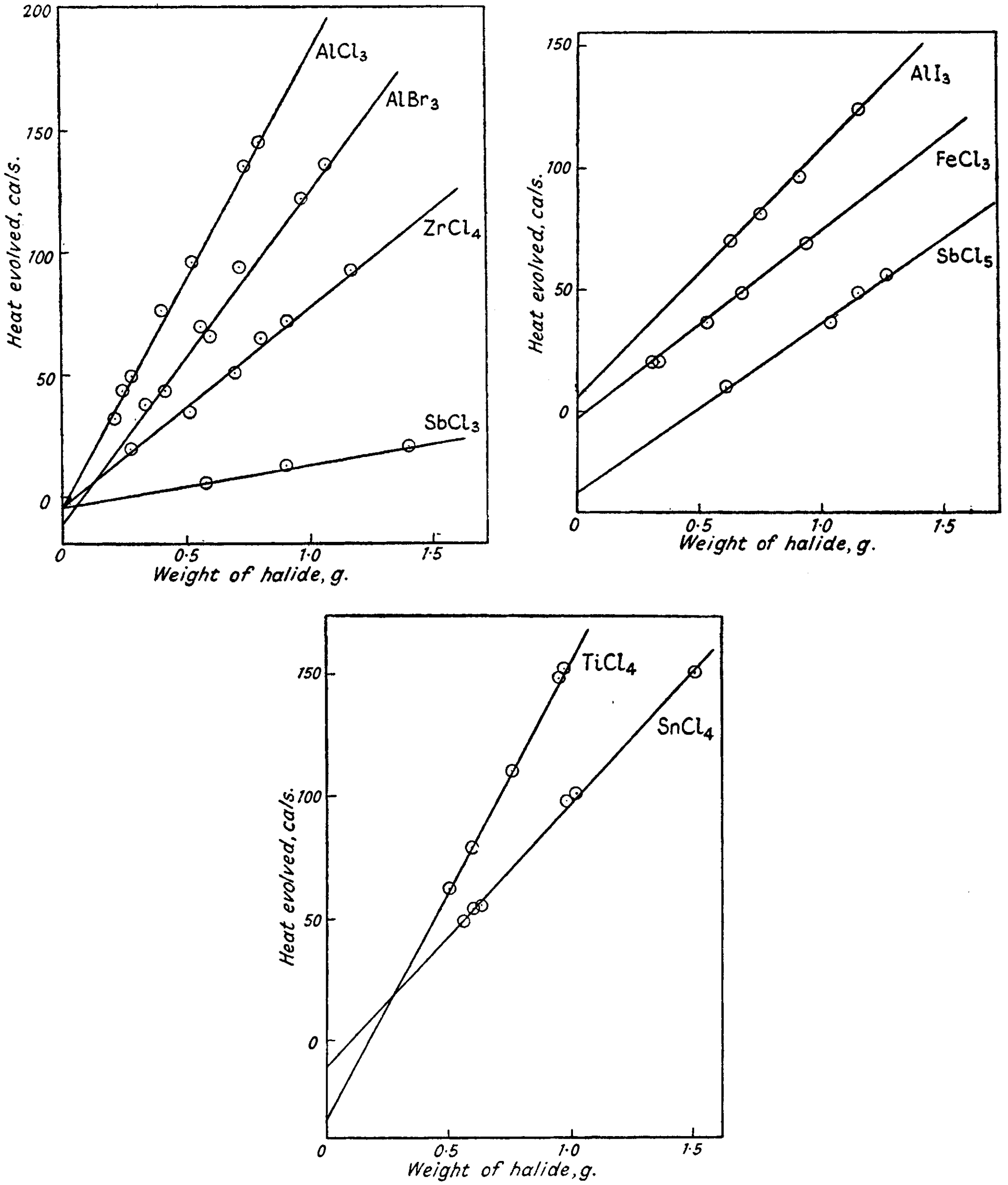
$$\tfrac{1}{2}Al_2Cl_6(s) + C_6H_5{\cdot}CHO(soln.) \longrightarrow C_6H_5{\cdot}CHO,AlCl_3(s) + 24{\cdot}7 \text{ kcals.}$$

We have not been able to crystallise this complex. The only reference to a benzaldehyde complex in the literature claims a crystalline compound, $C_6H_5{\cdot}CHO,AlCl_3,CH_3{\cdot}OH$, from methyl alcohol as solvent (Gangloff and Henderson, *J. Amer. Chem. Soc.*, 1917, **39**, 1420).

Some experiments were made which showed that neither hydrogen chloride nor water vapour had any marked effect. Thus, in run 165 the calorimetric liquid was chlorobenzene saturated with hydrogen chloride. The larger value of $Q$ = 28·9 kcals. may be attributed to the heat of solution of hydrogen chloride in benzaldehyde, but there was no other peculiarity. In runs 167 and 169 the chlorobenzene and aluminium chloride were stirred for 30 minutes and 10 minutes respectively with fine aluminium powder, to remove any free hydrogen chloride, before addition of benzaldehyde. The result, $Q$ = 24·7 kcals., was obtained. Similarly, nitrogen saturated with water (either at 0° or 40°) had no effect when passed through the calorimetric liquid during a run, apart from slight hydrolysis of the aluminium chloride.

FIG. 1*a*, *b*, *c*.

*Heats of mixing of metal halides with* 4·26 *g. of benzaldehyde.*



*Sodium aluminium chloride*, $NaAlCl_4$. Chlorobenzene was used as calorimetric liquid. The heat in this case was evolved during 15—30 minutes, that is, much longer than the usual 0·5—4 minutes required for complex formation. Only a trace of hydrogen chloride was evolved, so it is unlikely that there was any reaction between chlorobenzene, benzaldehyde, and sodium aluminium chloride. The resulting solution had a brown coloration and there was a dirty brown precipitate. The heat value gives $Q$ = 15 kcals. per mole of $NaAlCl_4$.

It seems very likely that complex formation occurs only after dissociation of the halide into sodium chloride and aluminium chloride. The heat of dissociation has been measured by Plotnikov (*J. Physical Chem. U.S.S.R.*, 1938, **12**, 113): $NaAlCl_4 \longrightarrow NaCl + AlCl_3 - 6{\cdot}6$ kcals. Assuming a zero heat of mixing of sodium chloride and benzaldehyde, we obtain 21·6 kcals. for the heat of formation of $C_6H_5{\cdot}CHO,AlCl_3$, which approaches the value obtained directly.

*Aluminium bromide.* Experiments were made with both chlorobenzene and bromobenzene as calorimetric liquids. It was found that addition of aluminium bromide to chlorobenzene gave a golden solution which deposited a considerable amount of resin on standing; there was also a small positive heat of mixing. A very feeble reaction has, in fact, been reported by Copisarow and Long (*J.*, 1921, **119**, 442). Addition of aluminium bromide to bromobenzene gave a clear cherry-red solution, accompanied by a small temperature rise. There is no reaction in this case, according to Copisarow and Long. Experiments 134—137 were with bromobenzene and 140—143 with chlorobenzene as calorimetric liquid. The results are all shown on the same graph in Fig. 1*a*. The intercept of approximately −12 cals. is larger than the heat of solution of 4·26 g. of benzaldehyde in 60 c.c. of chlorobenzene (−5 cals.) or bromobenzene (measured as −5·7 cals.). The difference is due either to a heat of solution of the complex or to loss of halide by hydrolysis during the run. Each run resulted in a red-brown clear solution indicating that the complex was at least partly soluble; a trace of hydrogen bromide was evolved in some cases. From the slope we have $Q = 36{\cdot}0$ kcals./mole of $AlBr_3$.

We assume, from molecular-weight determinations in benzene at similar concentrations (Ulich, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 423), that aluminium bromide is a dimer in solution in bromobenzene or chlorobenzene. We assume that the complex formed is 1 : 1, by analogy with aluminium chloride. Thus we have $\frac{1}{2}Al_2Br_6(soln.) + C_6H_5{\cdot}CHO(soln.) \longrightarrow C_6H_5{\cdot}CHO,AlBr_3(soln.) + 36{\cdot}0$ kcals.

*Aluminium iodide.* Chlorobenzene was used as calorimetric liquid. Addition of aluminium iodide to chlorobenzene gave only a very small rise in temperature with a slight red coloration, which a thiosulphate test showed to be due to a trace of free iodine. The end-product of these runs was a bright red solution with a red precipitate; the colour was probably due to liberated iodine.

The intercept gives a positive heat of 6 cals., which may be due to a liberation of some free iodine. The slope gives $Q = 42{\cdot}4$ kcals. per mole of $AlI_3$. Since aluminium iodide is only sparingly soluble in benzene, and since it is dimeric in the solid state (Wells, "Structural Inorganic Chemistry," Oxford, 1945), the system may be written $\frac{1}{2}Al_2I_6(s) + C_6H_5{\cdot}CHO(soln.) \longrightarrow C_6H_5{\cdot}CHO,AlI_3(s) + 42{\cdot}4$ kcals.

*Ferric chloride.* Chlorobenzene was used as calorimetric liquid. Addition of ferric chloride gave a small temperature rise with a slight yellow coloration; when kept for several days, most of the halide dissolved to give an orange solution. There is evidence (Thomas, *Compt. rend.*, 1898, **126**, 1211) that ferric chloride has a slow chlorinating action on chlorobenzene, but this is negligible during the time of a run. The end-product was a clear red solution in all cases and no hydrogen chloride was evolved. A few specks of unchanged ferric chloride could be detected, but addition of a further 1 c.c. of benzaldehyde gave no additional rise in temperature. The values are $S = -3$ cals.; $Q = 12{\cdot}8$ kcals. per mole of $FeCl_3$. Since ferric chloride is dimeric in the solid state (Wells, *op. cit.*) and only sparingly soluble in chlorobenzene we may write $\frac{1}{2}Fe_2Cl_6(s) + C_6H_5{\cdot}CHO(soln.) \longrightarrow C_6H_5{\cdot}CHO,FeCl_3(soln.) + 12{\cdot}8$ kcals.

*Ferric chloride and aluminium chloride.* For certain cases Martin, Pizzolato, and McWaters (*J. Amer. Chem. Soc.*, 1935, **37**, 2584) suggest a combined complex, *e.g.*, $C_6H_5{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3,AlCl_3,FeCl_3$. To examine this possibility for benzaldehyde, we investigated the addition of 4·26 g. of benzaldehyde to a mechanical mixture of the two halides. Col. 4, Table IV, gives the heat calculated from the previous values, assuming an additivity of action of the halides. It is seen to agree closely with the value observed. Clearly, there is no combined complex.

TABLE IV.

*Aluminium and ferric chlorides.*

| Run. | $AlCl_3$ (g.). | $FeCl_3$ (g.). | Calc. heat (cals.). | Obs. heat (cals.) |
|---|---|---|---|---|
| 161 | 0·279 | 0·317 | 84·0 | 85·7 |
| 162 | 0·683 | 0·083 | 139·5 | 140·1 |
| 163 | 0·235 | 0·661 | 103·5 | 104·4 |

*Stannic chloride.* Chlorobenzene was used as calorimetric liquid; stannic chloride dissolved in it with considerable absorption of heat to give a clear colourless solution. There was no evolution of hydrogen chloride on addition of benzaldehdye and the end-product was a white complex precipitated from a colourless solution. Pfeiffer (*Annalen*, 1910, **376**, 285) has previously isolated the complex as a white crystalline powder of formula $2C_6H_5{\cdot}CHO,SnCl_4$. This formula is borne out by our own work described later. The values are: $S = -10$ cals.; $Q = 28{\cdot}0$ kcals. per mole of $SnCl_4$. The equation can be written $SnCl_4(soln.) + 2C_6H_5{\cdot}CHO(soln.) \longrightarrow (C_6H_5{\cdot}CHO)_2,SnCl_4(s) + 28{\cdot}0$ kcals.

*Titanic chloride.* Chlorobenzene was used as calorimetric liquid. Addition of titanic chloride to this liquid gave an absorption of heat and a pale yellow colour, and there was no evidence of reaction. The end-product consisted of an orange precipitate and a yellow solution, a trace of hydrogen chloride being evolved. There is a very large intercept of −30 cals., which might be due to a considerable loss of this very easily hydrolysed halide in each run: $Q = 35{\cdot}0$ kcals. per mole of $TiCl_4$. By analogy with stannic chloride, and other titanic chloride complexes, we write

$$TiCl_4(soln.) + 2C_6H_5{\cdot}CHO(soln.) \longrightarrow (C_6H_5{\cdot}CHO)_2,TiCl_4(s).$$

*Antimony trichloride.* Chlorobenzene was used as calorimetric liquid. Addition of antimony trichloride to this liquid gave an absorption of heat and the halide rapidly dissolved to give a clear colourless solution, with no evidence of reaction. The complex was completely soluble, and no hydrogen chloride was evolved. We calculate: $S = -5$ cals.; $Q = 3{\cdot}9$ kcals. per mole of $SbCl_3$.

Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1929) has isolated the complex and found it to be $C_6H_5{\cdot}CHO,SbCl_3$. Thus the equation is

$$SbCl_3(soln.) + C_6H_5{\cdot}CHO(soln.) \longrightarrow C_6H_5{\cdot}CHO,SbCl_3(soln.) + 3{\cdot}9 \text{ kcals.}$$

*Antimony pentachloride.* When antimony pentachloride was added to chlorobenzene, there was a violent reaction with evolution of hydrogen chloride and a large temperature rise, the result being a clear, dark red solution. Dry benzene gave a similar result, the solution being almost black.

Addition of 5 c.c. of benzaldehyde to 60 c.c. of carbon tetrachloride gave a sudden fall in temperature, followed by a temperature rise attributed to oxidation of the benzaldehyde. The temperature rise was considerably reduced by addition of a trace of quinol, and the heat of solution was then measured as −24 cals.

Therefore carbon tetrachloride plus a trace of quinol was used as calorimetric liquid. The intercept is −32 cals., greater than the aforesaid heat of solution. The complex was obtained as a white precipitate from a pale green solution : $Q = 21{\cdot}0$ kcals. per mole of $SbCl_5$.

Rosenheim and Stellmann (*Ber.*, 1901, **34**, 3377) have found the complex to have the formula $C_6H_5{\cdot}CHO,SbCl_5$. Therefore $SbCl_5(soln.) + C_6H_5{\cdot}CHO(soln.) \longrightarrow C_6H_5{\cdot}CHO,SbCl_5(s) + 21{\cdot}0$ kcals.

*Zirconium tetrachloride.* Chlorobenzene was used as calorimetric liquid. Addition of powdered zirconium tetrachloride gave a small temperature rise, the result being a suspension indicating a negligible solubility of the halide. The end-product was a white precipitate settling from a yellow solution, a trace of hydrogen chloride being evolved in some cases. The graph gives $S = -5$ cals.; $Q = 18{\cdot}9$ kcals. per mole $ZrCl_4$.

Zirconium tetrachloride is monomeric in the solid state (Hansen, *Z. physikal. Chem.*, 1930, *B*, **8**, 1). It is known to form 2 : 1 complexes, *e.g.*, $(C_6H_5{\cdot}CO{\cdot}CH_3)_2,ZrCl_4$, which are said to be stable only at low temperatures (Jantsch, *J. pr. Chem.*, 1927, **115**, 7). The benzaldehyde complex is stable at 25°. The system is $ZrCl_4(s) + 2C_6H_5{\cdot}CHO(soln.) \longrightarrow (C_6H_5{\cdot}CHO)_2,ZrCl_4(s) + 18{\cdot}9$ kcals.

*Zinc chloride.* When 5 c.c. of benzaldehyde were added to powdered zinc chloride in chlorobenzene, the temperature rose slowly for about one hour and the rate was not increased by the addition of either water or hydrogen chloride. It is probable that slow complex formation was occurring, as is known to be the case with benzophenone (Reddelien, *Annalen*, 1911, **388**, 165).

*Boron trifluoride.* Some preliminary results were recorded with the etherate $(C_2H_5)_2O,BF_3$, which dissolved in chlorobenzene without reaction. Addition of 5 c.c. of benzaldehyde gave no rise in temperature, suggesting that there is negligible displacement of ether by benzaldehyde. Addition of pyridine (shown in another paper to give very stable complexes) gave a temperature rise corresponding to about 16 kcals./mole. Laubengayer and Findlay (*J. Amer. Chem. Soc.*, 1943, **65**, 885) give the heat of complex formation of the etherate as 12·5 kcals. per mole, and hence we conclude

$$C_5H_5N,BF_3 > 12{\cdot}5 \text{ kcals.} > C_6H_5{\cdot}CHO,BF_3.$$

*Beryllium chloride.* A slow temperature rise was observed when benzaldehyde was added to beryllium chloride in chlorobenzene, and most of the halide dissolved in about 4 hours, indicating slow complex formation.

*Ferrous chloride.* This was a pale green powder which did not dissolve in, or react with, chlorobenzene. On addition of benzaldehyde there was a slow rise in temperature as the halide dissolved to a golden solution.

*Calcium chloride, mercuric chloride, stannous chloride, and aluminium fluoride.* These halides gave no indication of complex formation with benzaldehyde at 25°.

*Hydrates* $FeCl_3,6H_2O$, $SnCl_4,5H_2O$, and $SnCl_2,2H_2O$. These gave no indication of complex formation with benzaldehyde at 25°.

*Cuprous chloride and cupric chloride.* Benzaldehyde added to cuprous chloride in chlorobenzene gave a slow temperature rise and formation of a blue-green colour. Cupric chloride gave only slight evidence for complex formation with benzaldehyde.

Some of the foregoing results are summarised below.

*Collected results on complex formation.*

| Halide. | $Q$, kcals./mole. | Halide. | $Q$, kcals./mole. | Halide. | $Q$, kcals./mole. |
|---|---|---|---|---|---|
| $AlI_3$ ………… | 42·4 | $AlCl_3$ ………… | 24·7 | $FeCl_3$ ……… | 12·8 |
| $AlBr_3$ ……… | 36·0 | $SbCl_5$ ……… | 21·0 | $BF_3$ ………… | ? |
| $TiCl_4$ ……… | 35·0 | $ZnCl_4$ ……… | 18·9 | $SbCl_3$ ……… | 3·9 |
| $SnCl_4$ ……… | 28·0 | | | | |

*Possible complex formation :* Beryllium chloride, zinc chloride, ferrous chloride, cuprous chloride.

*No complex formation :* Calcium chloride, mercuric chloride, stannous chloride, cupric chloride, aluminium fluoride.

*Errors.*—We have noted that the calorimetry itself is accurate to 1%. The biggest error in the work certainly lies in the handling of chemicals, especially in the transference of halides to the calorimeter. This error can only be estimated from the reproducibility of results as shown by the graphs, and varies with the different halides. In this light the values of $Q$ are probably accurate to ±1 kcal. This error is likely to affect the order in the above list only in the case of aluminium bromide and titanic chloride.

*Group II.*—In this series of experiments 60 c.c. of chlorobenzene were used as calorimetric liquid, and 0·804 g. (0·0076 mole) of benzaldehyde.

Consider the case where the halide $MX_n$ exists as a monomer and forms a 1 : 1 complex with benzaldehyde. If $a$ is the initial concentration of $MX_n$, $b$ of benzaldehyde, and $x$ is the concentration of complex formed at equilibrium, all concentrations being in moles/reaction volume, then an equilibrium constant may be written for the above equilibrium,

$$K = x/(a - x)(b - x) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

whence

$$x = \tfrac{1}{2}[a + b + 1/K \pm \sqrt{(a + b + 1/K)^2 - 4ab}\,] \quad . \ . \ . \ . \ . \ . \quad (3)$$

In the first place we have calculated this equation for the fixed value of $b = 0{\cdot}0076$ as used in our experiments, and a series of values of $K$, the results being shown in Fig. 2. For the higher values of $K$ the curve flattens out at $a = b$, $x$ approaching b.

In attempting to analyse a given experimental curve we assume that the amount of complex formed ($x$) is proportional to the amount of heat evolved in cals., $H$; *i.e.*, $x = cH$, so that

$$K = cH/(a - cH)(b - cH) \qquad (4)$$

Where $K$ is large and $b \gg a$, as in the Group I runs, we can replace $b - x$ by $b - a$ as an approximation, and

$$K = cH/(a - cH)(b - a) \qquad (5)$$

Thus, from two points ($H_1a_1$, $H_2a_2$) on a graph for Group I results, we can calculate $c$, since

$$c = [H_1a_2(b - a_2) - H_2a_1(b - a_1)]/H_2H_1(a_1 - a_2) \qquad (6)$$

Such a value of $c$ can then be used to obtain $K$ from Group I results and equation (4).

It is not possible accurately to allow for dissociation of a dimer such as $Al_2Cl_6$. Here we have two equations:

$$Al_2Cl_6 \rightleftharpoons 2AlCl_3 \quad (K_1)$$

$$AlCl_3 + C_6H_5{\cdot}CHO \rightleftharpoons C_6H_5{\cdot}CHO,AlCl_3 \quad (K_2)$$

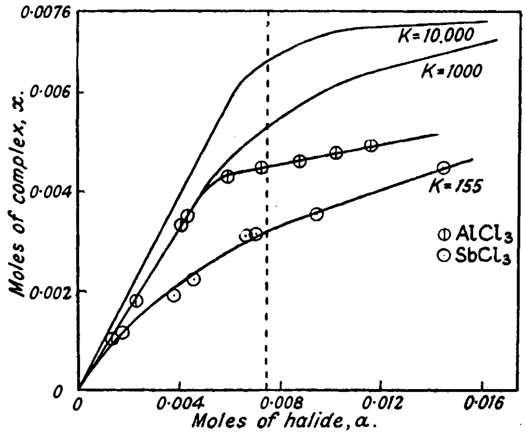
The " initial concentration " of $AlCl_3$ will be $\sqrt{K_1a}$, where $a = [Al_2Cl_6]$. Then equation (2) becomes

$$K_2 = cH/(\sqrt{K_1a} - cH)(b - cH) \qquad (7)$$

We have now two unknown constants $K_1$ and $K_2$ which are not obtainable without further information.

FIG. 2.

*Equilibrium curves for* $AlCl_3$ and $SbCl_3$–$C_6H_5{\cdot}CHO$ *systems.*



In a case like stannic chloride we have good reasons to expect $SnCl_4 + 2C_6H_5{\cdot}CHO \rightleftharpoons (C_6H_5{\cdot}CHO)_2,SnCl_4$. With the same symbols,

$$K = x/(a - x)(b - 2x)^2 \qquad (8)$$

It is possible to estimate $K$ from experimental data in the following manner. $K(a - x)$ is calculated for the actual $b$ value of $b = 0{\cdot}0076$ :

$$K(a - x) = x/(b - 2x)^2$$

Thus, we first tabulated $K(a - x)$ for a range of values of $x$ from 0·0001 to 0·0037. The maximum value of $x$ is $x = b/2$ We could then calculate the $x/a$ relation for a series of $K$ values, *viz.*, $K = 10^5, 10^6, 10^7$, and $10^8$. (These, of course, are chosen to cover the range required.) The $a$–$x$ curves are plotted in Fig. 3. In any actual case we can estimate $K$ to an order of magnitude by comparison of the observed curve with the form of the calculated curves.

It is clear that for the two higher values of $K$ the $a$–$x$ curve flattens out at $a = b/2 = 0{\cdot}0038$.

To summarise : (1) Group I experiments, $b \gg a$, enable us to calculate the proportionality constant $c$ for the heat evolved $H$; *i.e.*, $c = x/H$. (2) Group II experiments, $b \sim a$, together with the value of $c$ above, lead to a value of $K$. Additionally, at least in the case where $K$ is large, it should prove easy to determine the molecularity of benzaldehyde in the complex, since the curve of $H$ or $x$ against $a$ should flatten out at either $a = b$ for 1 mole or $a = b/2$ for 2 moles of benzaldehyde.

*Aluminium chloride.* In Fig. 4 we have the plot of $H$ against moles of $a$. These are obtained from the results of Group I by simply correcting for the heat of solution; that is, adjusting the graph so that it goes through the origin of co-ordinates. We have

$$a_1 = 0{\cdot}005;\ H_1 = 127{\cdot}2 \text{ cals.} \qquad a_2 = 0{\cdot}002;\ H_2 = 51{\cdot}2 \text{ cals.}$$

Substituting in equation (6), we obtain $c = 0{\cdot}0000361$ mole/cal. Substituting back in equation (4) for $a_1$ and $H_1$ gives $K = 314$.

Alternatively, it appears from Fig. 2, where we compare the theoretical curves for $b = 0{\cdot}0076$ and various values of $K$ with the experimental curve for $b = 0{\cdot}0076$, that $K \sim 1000$. With this value of $K$ we can construct $a$–$x$ curves from equation (2) for $b = 0{\cdot}0402$. The result is :

| | | | | | | |
|---|---|---|---|---|---|---|
| $a$ .............. | 0·001 | 0·002 | 0·005 | 0·01 | 0·015 | 0·02 |
| $x$ .............. | 0·001 | 0·00191 | 0·00486 | 0·00965 | 0·0143 | 0·019 |

Referring to the experimental graphs for $b = 0{\cdot}0402$ in Fig. 4, we obtain $a = 0{\cdot}005$ for $H = 127{\cdot}2$; whence $x = 0{\cdot}00486$, $H = 127{\cdot}2$, and $c = 0{\cdot}00486/127{\cdot}2 = 0{\cdot}0000382$ mole/cal. It is clear that the value of $c$ is rather insensitive to $K$ values.

The results of the runs with $b = 0{\cdot}0076$ are shown in Table V. The " corrected heats " are corrected for the heat of solution of the 1 c.c. of benzaldehyde in 60 c.c. of chlorobenzene.

TABLE V.

| Run. | Halide (g.). | $a$, moles. | Heat (cals.). | Heat, corr. (cals.). | $x$, moles. | $\Delta T$. |
|---|---|---|---|---|---|---|
| | | | *Aluminium chloride.* | | | |
| 57 | 0·191 | 0·00143 | 26·4 | 27·9 | 0·00103 | 0·0147° |
| 69 | 0·326 | 0·00244 | 48·0 | 49·5 | 0·00183 | — |
| 70 | 0·564 | 0·00423 | 84·7 | 90·2 | 0·00333 | — |
| 420 | 0·391 | 0·00293 | 62·4 | 63·9 | 0·00236 | — |
| 421 | 0·588 | 0·00441 | 91·9 | 93·4 | 0·00346 | 0·132 |
| 422 | 0·806 | 0·00605 | 113·4 | 114·9 | 0·00425 | 0·360 |
| 424 | 1·181 | 0·00886 | 121·3 | 122·8 | 0·00455 | 1·140 |
| 425 | 1·369 | 0·01027 | 125·9 | 127·4 | 0·00472 | 1·290 |
| 426 | 1·561 | 0·0117 | 130·2 | 131·7 | 0·00487 | 1·710 |
| 427 | 0·985 | 0·00739 | 118·4 | 119·9 | 0·00444 | 0·550 |
| | | | *Antimony trichloride.* | | | |
| 93 | 0·906 | 0·00398 | 4·8 | 6·3 | 0·00183 | 0·081 |
| 94 | 0·464 | 0·00204 | 2·4 | 3·9 | 0·00117 | 0·029 |
| 95 | 1·580 | 0·00692 | 9·3 | 10·8 | 0·00314 | 0·140 |
| 96 | 1·123 | 0·00493 | 6·1 | 7·6 | 0·00221 | 0·105 |
| 99 | 1·660 | 0·00728 | 9·2 | 10·7 | 0·00311 | 0·155 |
| 435 | 2·181 | 0·00958 | 10·6 | 12·1 | 0·00350 | 0·118 |
| 436 | 3·341 | 0·0147 | 14·0 | 15·5 | 0·00449 | 0·162 |
| 437 | 4·201 | 0·0184 | 17·2 | 18·7 | 0·00542 | 0·214 |
| | | | *Ferric chloride.* | | | |
| 81 | 0·373 | 0·00230 | 22·7 | 24·2 | 0·00165 | 0·081 |
| 84 | 0·454 | 0·00280 | 28·2 | 29·7 | 0·00202 | — |
| 85 | 0·698 | 0·00429 | 38·3 | 39·8 | 0·00271 | 0·31 |
| 88 | 0·825 | 0·00507 | 39·7 | 41·2 | 0·00280 | 0·36 |
| 89 | 1·232 | 0·00757 | 46·8 | 48·3 | 0·00328 | 0·86 |
| 90 | 1·365 | 0·00840 | 47·5 | 49·0 | 0·00334 | 1·05 |
| 91 | 0·249 | 0·00154 | 15·4 | 16·9 | 0·00115 | 0·059 |
| 92 | 1·740 | 0·0107 | 47·7 | 49·2 | 0·00335 | 1·23 |
| | | | *Stannic chloride.* | | | |
| 100 | 1·092 | 0·00419 | 102·5 | 104·0 | 0·00348 | 0·096 |
| 101 | 1·604 | 0·00616 | 107·0 | 108·5 | 0·00363 | 0·59 |
| 102 | 0·720 | 0·00277 | 74·2 | 75·7 | 0·00253 | 0 |
| 103 | 0·484 | 0·00186 | 44·7 | 46·2 | 0·00154 | 0 |
| 428 | 1·701 | 0·00653 | 107·9 | 109·4 | 0·00366 | 0·97 |
| 429 | 1·032 | 0·00395 | 99·5 | 101·0 | 0·00338 | 0·015 |
| 430 | 1·255 | 0·00482 | 113·2 | 114·7 | 0·00384 | 0·29 |
| 431 | 1·419 | 0·00545 | 116·1 | 117·6 | 0·00393 | 0·49 |
| 432 | 2·157 | 0·00830 | 108·4 | 109·9 | 0·00368 | 1·55 |
| 433 | 2·390 | 0·00916 | 118·2 | 119·7 | 0·00400 | — |
| 434 | 0·586 | 0·00225 | 55·3 | 56·8 | 0·00189 | 0 |

The last column, $\Delta T$, is a measure of the temperature rise when a second c.c. of benzaldehyde was added. It indicates how far the original reaction had gone to completion.

In Fig. 2 we show a graph of $a$ against $x$ for $b = 0{\cdot}0076$, and it is clear that until the equivalence point $a = b$ is approached, the curve follows closely the theoretical $K = 1000$. Near the equivalence point the experimental curve flattens out abruptly and $x$ is too small for a given value of $a$. This may well be due to lack of the dimerisation term and really we should use equation (7), which, as we have already mentioned, cannot be solved. A semi-empirical method may be used. The heat of dissociation of $Al_2Cl_6$ is 28 kcals. per mole. We assume complete dissociation of $Al_2Cl_6$ to $2AlCl_3$ up to the equivalence point $b = 0{\cdot}0076$. Up to this value we must therefore *add* on the heat of dissociation to provide corrected values for $AlCl_3 + C_6H_5{\cdot}CHO \longrightarrow C_6H_5{\cdot}CHO,AlCl_3$. Above this value we may neglect any further dissociation of $Al_2Cl_6$. After correcting the curve for 0·042 mole of benzaldehyde in this way we calculate $c = 0{\cdot}000024$ mole/cal. This result has been used to calculate curve $b$ in Fig. 5.

If $K = 1000$, then the true value of $K$, $K_t$, is $KV$, where $V = 0{\cdot}06$ litre, the volume of the reaction space. This gives $\Delta G^\circ = -\boldsymbol{R}T \ln K_t = -2440$ cals. (298° K.) and hence $\Delta S = -75$ cal. deg.$^{-1}$mole$^{-1}$, which seems very large. The values of $\Delta G^\circ$ and $\Delta S^\circ$ so calculated correspond to the concentrations, in moles per litre, in the equilibrium constant. By flattening out at $a = b$, the experimental curve strongly supports the idea of a 1 : 1 complex.

FIG. 3.

*Equilibrium curves for* $(C_6H_5{\cdot}CHO)_2,SnCl_4$ *complex.*

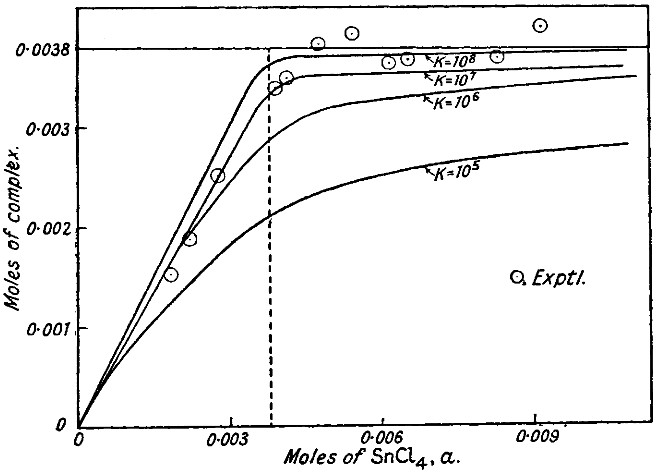


FIG. 4.

*Corrected heats of mixing of metal halides with 4·26 g. of benzaldehyde.*

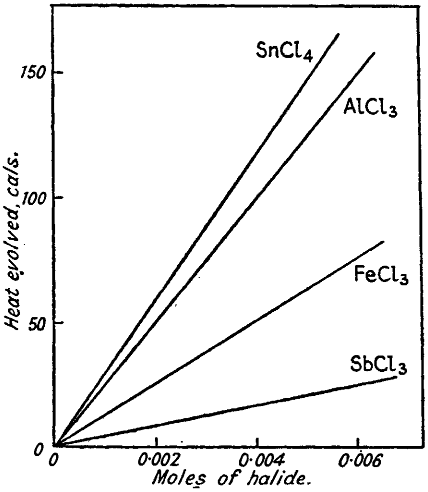
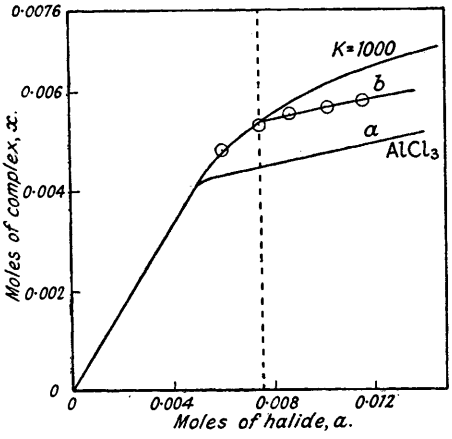


FIG. 5.

*Equilibrium curves :*

(a) $AlCl_3 + C_6H_5{\cdot}CHO \longrightarrow C_6H_5{\cdot}CHO{\cdot}AlCl_3$.

(b) *With allowance for the dissociation* $Al_2Cl_6 \longrightarrow 2AlCl_3$.



*Antimony trichloride.* From the Group I, $b = 0{\cdot}0402$, runs in Fig. 4, we calculate $c = 0{\cdot}000294$ mole/cal. We have used this value to derive $x$ from $H$ in the runs with $b = 0{\cdot}0076$, given in Table V, and hence to plot a graph of $x$ against $(a - x)$ $(b - x)$ in Fig. 6. An approximate straight line results, and from the slope $K = 155$. Using equation (2), we can then calculate the $x$–$a$ curve with the values of $c$ and $K$ already determined, and the theoretical curve in Fig. 2 is seen to agree closely with the experimental curve. This analysis gives strong support to the idea of a 1 : 1 complex. We may calculate $\Delta G^\circ = -\boldsymbol{R}T \ln K_t = -1300$ cals., to compare with the previously measured $\Delta H = -3900$ cals.

*Ferric chloride.* The constant $c$ is found from Fig. 4 for $b = 0{\cdot}0402$, in the same way as for aluminium chloride. We have $c = 0{\cdot}000068$ mole/cal.

The runs for $b = 0{\cdot}0076$ are shown in Table V, and plotted in Fig. 7. According to the initial slope, the ferric chloride curve should have $K \sim 500$, but in fact it falls much below this, flattening out at the 1 : 1 ratio of ferric chloride to benzaldehyde. Since ferric chloride is known to exist as the dimer, the reason is probably the same as for aluminium chloride, but in the absence of a knowledge of the heat of dissociation it is not worth while to try to apply a correction.

*Stannic chloride.* As for aluminium and antimony chlorides, we first calculate $c$ from the experimental curve of Fig. 4 for $b = 0{\cdot}0402$. Two points are taken :

$$a_1 = 0{\cdot}004;\ H_1 = 117{\cdot}5 \qquad a_2 = 0{\cdot}002;\ H_2 = 59{\cdot}0$$

and $c$ calculated from $K = cH/(a - cH)\,(b - 2a)^2$, whence $c = 0{\cdot}0000334$.

The heat values for $b = 0{\cdot}0076$ are shown in Table V, together with derived values of $x$. In Fig. 3 we compare the experimental $x$–$a$ curve with theoretical curves for various $K$ values. Agreement is found with the cases where $K = 10^8$—$10^9$. This high $K$ value is borne out by the fact that addition of a second c.c. of benzaldehyde gives no further heat evolution until the equivalence point ($a = 0{\cdot}0038$ mole) is passed. The agreement bears out that the complex is $(C_6H_5{\cdot}CHO)_2,SnCl_4$.

FIG. 6.

*Complex formation between* $SbCl_3$ *and* $C_6H_5{\cdot}CHO$.

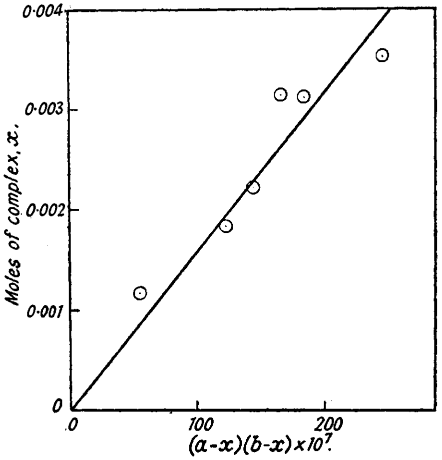
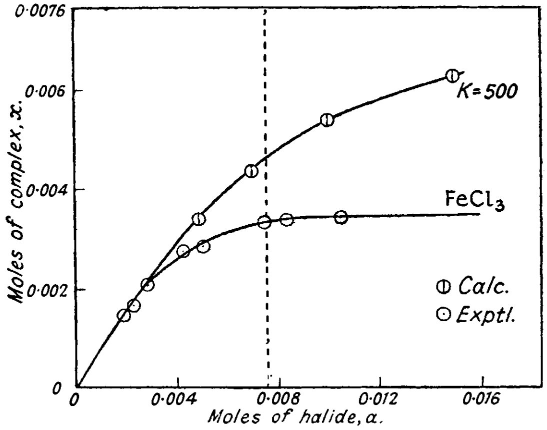


FIG. 7.

*Equilibrium curves for*
$FeCl_3 + C_6H_5{\cdot}CHO \longrightarrow C_6H_5{\cdot}CHO,FeCl_3$.



We may calculate $\Delta G^\circ = -\boldsymbol{R}T \ln K_t = -\boldsymbol{R}T \ln KV^2 \sim -7600$ cals., to be compared with $\Delta H = -28{,}000$ cals. The corresponding $\Delta S$ value of about $-68$ cals. per degree per mole is very high, but not unreasonably so as in the aluminium chloride case, since the freedom of motion of two benzaldehyde molecules is effectively frozen out in the complex.

## DISCUSSION.

The experiments of Group II may be regarded as substantiating our assumptions about the molecularity of the complexes, as already given in the description of the Group I experiments. The agreement between the observed curves and curves calculated on the basis of an equilibrium gives ample support to the notion that the complex is very slightly dissociated in chlorobenzene solution : $C_6H_5{\cdot}CHO + MX_n \rightleftharpoons C_6H_5{\cdot}CHO,MX_n$.

In the case of stannic chloride and antimony trichloride, excellent agreement is obtained between observed and calculated curves. For aluminium and ferric chlorides the agreement is not so good in that the experimental curve flattens out (at the equivalence point) more than theory would lead one to expect. The effect in these two cases is probably in part due to the neglect of the primary stage $(MX_n)_2 \rightleftharpoons 2MX_n$.

The value for the equilibrium constant $K$ from the Group II experiments is probably a lower value, and the method can only give at best the order of magnitude of $K$. Table VI shows that the catalysts in order of $K$ values agree with the order of the $\Delta H^\circ$ values, but that the $\Delta S^\circ$ values derived from $(\Delta H^\circ - \Delta G^\circ)/T$ are excessively high in the case of aluminium chloride, since the total third-law entropy of benzaldehyde per mole is only 57 cals.

TABLE VI.

| Complex. | $-\Delta H$, kcals. | $K$. | $K_t$. | $-\Delta G^\circ$, kcals. | $-\Delta S^\circ$, kcals. |
|---|---|---|---|---|---|
| $(C_6H_5{\cdot}CHO)_2,SnCl_4$ ............ | 28·0 | $\sim 10^8$ | $3{\cdot}6 \times 10^5$ | 7·6 | 68 |
| $C_6H_5{\cdot}CHO,AlCl_3$ ............... | 24·7 | $\sim 10^3$ | 60 | 2·4 | 75 ? |
| $C_6H_5{\cdot}CHO,FeCl_3$ ............... | 12·8 | $\sim 500$ | 30 | 2·0 | 36 |
| $C_6H_5{\cdot}CHO,SbCl_3$ ............... | 3·9 | $\sim 150$ | 9 | 1·3 | 9 |

These data, in spite of the large uncertainties in $\Delta G$, enable us to see that the formation of the benzaldehyde complex will make more favourable the free-energy change in the Gattermann–Koch reaction. At the same time, the large negative values of $\Delta H$, which are known accurately, show that the equilibrium yield of benzaldehyde may be expected to decrease strongly with rise in temperature.

For aluminium chloride we can calculate a new set of equilibrium constants based on the *total* free-energy change. Equation (1) is used without including the specific heat terms, and corresponding yields are obtained as follows. Consider the overall reaction,

$$C_6H_6 + CO + \tfrac{1}{2}Al_2Cl_6 \rightleftharpoons C_6H_5{\cdot}CHO,AlCl_3$$

If $a$ and $b$ are the initial concentrations of benzene and aluminium chloride respectively in moles/litre and $x$ is the concentration of complex formed, $KP_{CO} = x/(a - x)(b - x)$ where $P_{CO}$ is the partial pressure of carbon monoxide. In Part II, experiments are carried out under the following conditions: $a$ (pure benzene) $= 11{\cdot}4$ moles/litre, $b = 0{\cdot}667$ mole/litre, $P_{CO} = \frac{2}{3}$ atm. Hence the above equation approximates to $KP_{CO} = x/a(b - x)$. From this, $x$ is easily calculated and hence the mole-% yield based on aluminium chloride, *i.e.*, $100x/b$. The results are tabulated in Table VII. This shows that a very high yield is possible with aluminium chloride at room temperature although there is probably considerable error in the values quoted for the total free-energy change. A similar calculation at 298° K. gives for stannic chloride ≏100%; ferric chloride, 88%; and antimony trichloride 68·5% yields.

TABLE VII.

*Calculated equilibrium constants and yields for aluminium chloride.*

| | | | |
|---|---|---|---|
| $T$, °K. | 298 | 323 | 373 |
| $\Delta G^\circ$ | −380 | 2360 | 7630 |
| $K$ | 1·9 | 0·026 | $3{\cdot}6 \times 10^{-5}$ |
| Yield, % | 93·5 | 16·5 | 0·027 |

It is further possible to obtain on certain assumptions the energy $E$ of formation of the bond between benzaldehyde and the halide, in the gas phase, that is, the bond energy. The following cycle is used for aluminium chloride, and appropriately modified cycles are used for those halides which do not exist as dimers, or which take up two molecules of benzaldehyde.

$$\begin{tikzcd}
Al_2Cl_6(s) \arrow[d, "a"'] & + & 2C_6H_5{\cdot}CHO(soln.) \arrow[d, "-2b"'] \arrow[r, "2Q"] & 2C_6H_5{\cdot}CHO,AlCl_3(s) \arrow[dd, "2c"] \\
Al_2Cl_6(g) \arrow[d, "D"'] & & 2C_6H_5{\cdot}CHO(l) \arrow[d, "2d"'] & \\
2AlCl_3(g) & + & 2C_6H_5{\cdot}CHO(g) \arrow[r, "2E"] & 2C_6H_5{\cdot}CHO,AlCl_3(g)
\end{tikzcd}$$

where $Q$ = measured heat of complex formation, $D$ = heat of dissociation of $Al_2Cl_6$, $E$ = bond energy of $C_6H_5{\cdot}CHO{-}AlCl_3$, $a$ = heat of sublimation of $Al_2Cl_6$, $b$ = heat of solution of $C_6H_5{\cdot}CHO$ in $C_6H_5Cl$, $d$ = heat of evaporation of $C_6H_5{\cdot}CHO$, and $c$ = heat of sublimation of complex (neglecting any partial solution of the complex).

Then $2E = 2Q + a + 2d - 2b + D - 2c$.

We may neglect $b$. Although $a$ (27 kcals.) and $d$ (9 kcals.) are considerable, one can only assume at present that they tend to cancel the unknown term $c$ (Mr. H. Watts in our laboratory is endeavouring to measure this in the more suitable case of pyridine–aluminium chloride). Then approximately $E = Q + D/2$.

Smits and Meijering (*Z. physikal. Chem.*, 1938, *B*, **41**, 98) have found for aluminium chloride $D$ = 28 kcals. Fischer and Rahlfs (*Z. anorg. Chem.*, 1932, **205**, 1) found $D$ = 26·5 kcals. for aluminium iodide. Since ferric chloride vapour dissociates at a comparable temperature to aluminium chloride (Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," London, 1935, Vol. 14, p. 46), we assume the same $D$, *i.e.*, 28 kcals. In this way we have calculated the following table of bond energies.

*Bond energy of complex.*

| Halide. | Bond energy (kcals.). | Halide. | Bond energy (kcals.). | Halide. | Bond energy (kcals.) |
|---|---|---|---|---|---|
| $AlI_3$ | 54 | $FeCl_3$ | 27 | $SnCl_4$ | 14 |
| $AlBr_3$ | 49 | $SbCl_5$ | 21 | $ZrCl_4$ | 9 |
| $AlCl_3$ | 39 | $TiCl_4$ | 17 | $SbCl_3$ | 4 |

Later we propose to discuss these values in terms of the nature of the co-ordinate link, but at present our main interest is to use them in a discussion of kinetic data.

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