that chlorine attached to carbon will denote a pair of electrons to free chlorine. The purpose of the current investigation was to determine whether or not chlorides, in which the chlorine was attached to a more electropositive element than carbon, would also form solvates with free chlorine.

In the present investigation of the freezing point *vs.* concentration equilibria in the system of hydrogen chloride–chlorine, the experimental procedure was substantially identical with that employed in the study of the system of methyl chloride–chlorine.[2] The data obtained are presented in Table I and are plotted in Fig. 1.

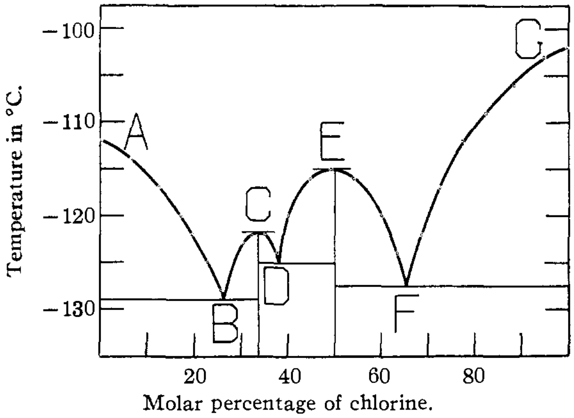

Fig. 1.—Freezing point *vs.* composition in system of hydrogen chloride–chlorine.

From the foregoing data it may be concluded that chlorine forms two solvates (chlorinates) with hydrogen chloride, whose empirical formulas and congruent melting points are as follows: (1) hydrogen chloride hemichlorinate, $(HCl)_2{:}Cl_2$, −121°; (2) hydrogen chloride monochlorinate, $HCl{:}Cl_2$, −115°.

Nothing concerning the structure of these compounds can be deduced from these data, but the authors venture the statement that it seems probable that hydrogen chloride should be combined with free chlorine by a coördinate covalent link. Since the hydrogen–chlorine link in hydrogen chloride is more polar than the chlorine–chlorine link in the free chlorine, the chlorine attached to hydrogen probably donates a pair of electrons which is accepted by the free chlorine. The structural formulas would therefore be

$$(1)\quad H{-}Cl \longrightarrow Cl{-}Cl \longleftarrow Cl{-}H$$
$$(2)\quad H{-}Cl \longrightarrow Cl{-}Cl$$

In conformity with the definition of perchlorides proposed in the second article of the current series,[2] the compounds identified during this investigation may be considered as perchlorides of hydrogen whose empirical formulas are H_2Cl_4 and HCl_3.

Summary

Two chlorinates of hydrogen chloride or perchlorides of hydrogen, have been identified and their congruent melting points determined.

ITHACA, N. Y. RECEIVED APRIL 5, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Chlorides of Gallium

BY A. W. LAUBENGAYER AND F. B. SCHIRMER

The formation of compounds by gallium has been shown to present numerous interesting problems, both of valence state and of molecular configuration. While trivalency, which is to be expected for this atom, is well established, the molecular species and configuration of the compounds in this state have not been well understood. Gallium also has been reported[1] to show divalence, a condition which cannot be reconciled with its atomic structure, and univalence, which should be possible due to the use of only the 4*p* electron for bonding purposes. Very little work is available about these lower valence states.

The system gallium–chlorine is a favorable one to study because gallium–chlorine bonds are strong enough to ensure reasonably stable molecules and the volatility of the chlorides makes it possible to investigate them in the vapor phase.

Gallium trichloride has been shown[1] to resemble aluminum chloride closely, being associated at lower temperatures. While a recent vapor pressure and density investigation[2] of this compound has given considerable data, this work does not agree on a number of points with the reports of earlier investigators, the temperature range cov-

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(1) L. de Boisbaudran, *Compt. rend.*, **93**, 294 (1881).

(2) Fischer and Jubermann, *Z. anorg. allgem. Chem.*, **227**, 227 (1936).

ered is not extensive enough to afford all the desired information, and the interpretation of the data is incomplete.

Gallium dichloride was prepared by de Boisbaudran[1] and other workers[3] by the reduction of gallium trichloride with hot gallium, but the conditions for preparation have not been well established, the purity of the product seems to have been considerably in doubt, and its properties have not been completely surveyed.

No reduction of gallium dichloride to a monochloride has been demonstrated, although Nilson and Pettersson suggested that a brownish colored film which remained on the walls of the glass reaction tube after reduction of the trichloride with excess gallium might have been the monochloride.

In the present investigation vapor phase studies of gallium trichloride over an extended temperature range have been undertaken. Pure gallium dichloride has been prepared and its properties, especially its behavior in the vapor phase, have been investigated. The possibility of obtaining gallium monochloride has been examined.

Apparatus and Procedure for Vapor Studies.—Because the system gallium–chlorine is very reactive, especially toward water and oxygen, the apparatus shown in Fig. 1, constructed completely of Pyrex glass, was used for vapor pressure and density measurements. This apparatus employed the vapor pressure cell A which had a glass manometer of the "sickle" type,[4] similar to a Bourdon gage. The cell could be connected by means of an interchangeable ground glass joint to the chain equipped with a mercury manometer, a McLeod gage, a vacuum pump, and drying tubes through which air could be admitted. The volume of the cell was determined by weighing it empty and then filled with water to the points on tubes B and C where they later would be sealed off. Corrections for change of volume with temperature were calculated.

The glass ampule containing the sample was scratched with a file, weighed, and introduced into the cell through tube B, which then was sealed off. The cell was attached to the chain, C was connected to D by glass and rubber tubing, and the cell was completely evacuated simultaneously on both sides of the sickle. C was sealed off and the zero positions of the pointers E and F were noted by means of a telescope. S_1 was closed, the cell was taken from the chain and shaken to break the sample tube, and then was reattached, and the chain beyond S_1 was evacuated. The temperature of the sample was controlled by immersing the cell to its side arm in a suitable thermostat. As the pressure in the cell rose the pointers were balanced approximately by admitting air through S_5 and S_1. When equilibrium at a given temperature was attained the pointers E and F were brought to their zero positions by manipulating the pressure of air, and this pressure was then read on the mercury manometer and corrected to give the pressure of the sample. To be sure that equilibrium was realized, the pressures corresponding to given temperatures were determined, both as the temperature was progressively raised and as it was lowered. By varying the size of the cell and the weights of sample used, accurate vapor pressure and density data could be secured over a wide temperature range. The apparatus and method were shown to be satisfactory by making measurements on pure aluminum chloride.

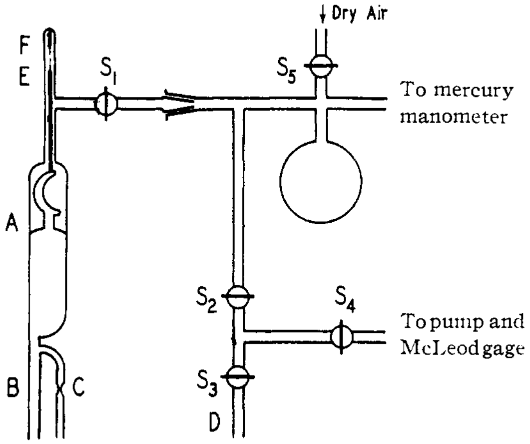

Fig. 1.

Study of Gallium Trichloride

Preparation and Analysis.—Gallium trichloride was prepared by the action of chlorine diluted with nitrogen on hot gallium. The product was distilled in a stream of nitrogen to remove the excess chlorine and further purified by sublimation *in vacuo*. It was analyzed by putting it into solution in 1% nitric acid and determining the gallium as the oxide and the chlorine as silver chloride.[5]

Anal. Calcd. for $GaCl_3$: Ga, 39.59; Cl, 60.41. Found: Ga, 39.55; Cl, 60.35.

Vapor Pressure of Gallium Trichloride.—Measurements were made in the temperature range 50 to 200°. The data for duplicate runs agree satisfactorily and are summarized in Table I. They check those reported by Fischer and Jubermann[2] but also cover a lower temperature range and thus give more information about the solid–vapor equilibrium.

The values of log p plotted against $1/T$ give solid–vapor and liquid–vapor lines which intersect at 77°, the melting point. The points for the liquid–vapor equilibria give a smooth slightly curved line, indicating a small change in the heat of vaporization with temperature. The thermal data for gallium trichloride calculated on the basis of these measurements are summarized in Table II and are compared with the values previously reported.

Vapor Density of Gallium Trichloride.—To determine the maximum association possible in

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[3] (a) Nilson and Pettersson, *Z. physik. Chem.*, **2**, 668 (1888); (b) Muscher and Wehrli, *Helv. Phys. Acta*, **7**, 332 (1934).

[4] Phipps, Spealman and Cooke, *J. Chem. Education*, **12**, 321 (1935).

[5] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929.

TABLE I

VAPOR PRESSURES OF GALLIUM TRICHLORIDE

Temp., °C. (±0.1°)	$1/T \times 10^3$	p, mm. Hg (±0.1)	Log p
50.0	3.095	1.2	0.079
55.1	3.047	1.9	.279
60.1	3.001	2.8	.447
65.1	2.957	4.3	.633
70.2	2.913	6.0	.778
75.1	2.872	8.5	.929
80.1	2.831	11.8	1.072
90.1	2.753	19.1	1.281
100.1	2.680	28.9	1.461
109.9	2.611	44.4	1.647
120.1	2.543	65.5	1.816
130.4	2.478	94.5	1.975
140.6	2.417	134.6	2.129
151.0	2.375	189.3	2.277
161.3	2.302	260.4	2.416
171.3	2.250	351.4	2.546
181.4	2.200	465.9	2.668
191.2	2.154	608.5	2.784
200.8	2.110	771.7	2.888

TABLE II

THERMAL DATA FOR GALLIUM TRICHLORIDE

	Other Investigators					The Authors
Melting point, °C.	75.5[1]	78.0[6]	76.65[7]	77.9[2]	76[9]	77.0
Boiling point, °C. (760 mm.)	215–220[1]	205[6]	199.6[7]	201.3[2]		200.0
Heat of vap. at b. p., kcal.	10.5[2]					11.4
Heat of vap. at m. p., kcal.	12.3[2]					11.8
Heat of subl. at m. p., kcal.	9.2[8]					17.0
Heat of fusion at m. p., kcal.						5.2

the vapor phase, measurements were made between 117 and 177°, as low a temperature range as was practical to use. No evidence was obtained for association beyond the dimer, Ga_2Cl_6.

To follow the dissociation of the dimeric molecule, further vapor density measurements were made between 177 and 498°, the highest temperature to which the glass sickle could be heated without undergoing permanent distortion. Establishment of equilibrium and absence of any decomposition of the sample was proved by rechecking the data as the cell cooled. The results for a sample weighing 0.5763 g., measured in a cell of 223.4 cc. capacity, are given in Table III. The apparent molecular weight, the fraction α of the dimeric molecules dissociated according to the equation $Ga_2Cl_6 \rightleftarrows 2\,GaCl_3$, and the logarithm of the equilibrium constant K_p are tabulated for each temperature.

Log K_p plotted against $1/T \times 10^3$ gives a very smooth curve which is not a straight line, the slight curvature being real and indicating a difference in the heat capacity of the two molecular species present. The heat of dissociation, calculated from the slope of the line at 365° where the dissociation is about 50%, is about 20 kilocalories. The dissociation of the saturated gallium trichloride vapor at its b. p., 200°, is only 1.5%. A second run on a sample of 0.7365 g. in the same cell gave temperature–log K_p values which check very closely with those listed in Table III. The data agree well with the results reported by Fischer and Jubermann[2] for the range above 258°. They reported a heat of dissociation of 21 kilocalories calculated from a straight line representing log K_p plotted against $1/T \times 10^3$, but when their data are replotted clear evidence for the slight curvature noted in the present investigation is apparent.

Electron diffraction studies of gallium trichloride vapor in the temperature range in which it has been shown to be at least 98% dimeric are in progress to determine the configuration of the molecule, Ga_2Cl_6.

TABLE III

EQUILIBRIUM OF Ga_2Cl_6 AND $GaCl_3$

Temp., °C. (±0.5)	$1/T \times 10^3$	Pressure, mm. (±0.2)	Obsd. mol. weight	α	Log K_p
177.5	2.219	206.7	351.2	0.0029	−2.155
205.5	2.089	226.4	340.5	.0344	+0.027
232.2	1.979	245.6	331.3	.0631	0.592
264.3	1.861	279.3	309.8	.1369	1.330
298.5	1.749	324.0	283.9	.2406	1.901
329.5	1.659	373.0	259.9	.3552	2.333
364.7	1.568	436.2	235.2	.4974	2.759
395.7	1.495	493.9	217.7	.6177	3.086
430.1	1.422	558.3	202.4	.7400	3.432
463.0	1.359	611.4	193.5	.8201	3.701
498.3	1.296	662.5	187.1	.8826	3.971

Study of Gallium Dichloride

Preparation and Analysis.—Gallium trichloride was held during a period of one hour at 175° with an excess of gallium in an evacuated Pyrex reaction tube. The dichloride which formed was heated to 225° and distilled away from the non-volatile impurities. During the distillation some decomposition occurred, gallium trichloride condensing with the dichloride in the cooler portions of the tube and gallium remaining behind. This decomposition, however, was not very serious and a good yield of dichloride was obtained. The section of the tube containing the chlorides was sealed off and placed in an-

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(6) Klemm and Tilk, *Z. anorg. allgem. Chem.*, **207**, 163 (1932).

(7) Craig and Drake, THIS JOURNAL, **56**, 584 (1934).

(8) Klemm, *Z. physik. Chem.*, **B12**, 17 (1931).

(9) Johnson, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, 1939, p. 27.

other glass tube which was evacuated and sealed. The tube containing the mixed chlorides was broken and the dichloride was purified by holding it at 160° and distilling off the more volatile trichloride. When most of the trichloride had been removed, the tube was cooled and the dichloride, which cracks away from the glass on cooling when fairly pure, was powdered by shaking. This powder was heated to 160° and the last traces of trichloride were driven to the cool end of the tube and sealed off. The pure gallium dichloride remaining was transferred and subdivided *in vacuo*, either by pouring the loose powder or by carefully melting it and allowing the liquid to flow. If the temperature was not raised much above the melting point, 170°, no appreciable decomposition occurred.

For analysis a weighed tube containing gallium dichloride was broken under 2% nitric acid. When the sample reacted with the nitric acid a small amount of gallium always formed. The solution was filtered and the gallium and fragments of glass were collected. The gallium and chlorine in the filtrate were determined as in the analysis of gallium trichloride. The metallic gallium was dissolved in aqua regia and precipitated as the hydroxide, which was added to that obtained from the main precipitation. The weight of the glass was determined and the weight of sample used was obtained by difference.

Anal. Calcd. for $GaCl_2$: Ga, 49.58; Cl, 50.42. Found: Ga, 49.42; Cl, 50.41.

The analytical results show that a chloride having a gallium–chlorine atomic ratio of 1 to 2 is secured by reduction of gallium trichloride under the conditions outlined, and that this compound can be freed completely of contaminating trichloride. No evidence of the formation of a monochloride in the presence of a large excess of gallium was observed.

Properties of Gallium Dichloride.—Gallium dichloride forms colorless crystals which were found to melt at 170.5 ± 0.5°, considerably higher than the value 164° reported by de Boisbaudran.[1] It is very probable that he did not have the pure substance. Liquid gallium dichloride does not wet glass readily but forms small droplets in the tube. The density of the liquid is greater than that of Pyrex glass, since fragments of the sample tubes were observed to float on the melt. The transparent colorless crystals which formed when gallium dichloride froze became opaque on further cooling and, in some cases, the movement through the solid of what appeared to be a crystalline boundary was observed. Single transparent crystals, grown by sublimation just below the melting point, were chilled quickly and were observed under the microscope to slowly become opaque. The evidence indicates that the solid is dimorphic and that the inversion is reversible, but attempts to determine the transition point were not conclusive. This transition is, however, not at all the same phenomenon as that reported by de Boisbaudran[1] as evidence of dimorphism of gallium dichloride. As will be pointed out later, the formation of a colored product when the dichloride is heated, which he mentioned, is satisfactorily explained by the formation of tiny droplets of gallium due to thermal decomposition.

Gallium dichloride deliquesces to give a thick sirupy colorless solution when exposed to the air. If it is placed in water a dark chocolate-brown solid precipitates. This solid slowly reacts with the water to give a gas, probably hydrogen, and the solid turns white, presumably forming gallic hydroxide. The liberation of a gas with an offensive odor, reported by de Boisbaudran and thought by him to be gallium hydride, was not observed in this investigation.

Gallium dichloride was found to dissolve readily in benzene with no apparent chemical interaction. It reacted with carbon tetrachloride and a black solid formed. This solid was insoluble in water, hydrochloric acid, and aqua regia and appeared to be carbon. Gallium dichloride is a powerful reducing agent.

In order to study the thermal stability of gallium dichloride, a sample in one end of an evacuated tube was heated and the other end of the tube was kept cool. Heating at 180° for three hours caused no change in the sample. At 200° a few small crystals of gallium trichloride collected in the cool end of the tube during one hour and, when the dichloride was cooled, a slight grayish color due to the formation of gallium was apparent in the solid. At still higher temperatures the decomposition to gallium and gallium trichloride was more rapid and globules of gallium were observed to form. When the dichloride was heated in Pyrex glass for some time at 500° the surface of the glass very slowly turned brown. The brown film could not be removed by aqua regia nor a mixture of nitric and chromic acids. These reagents would have reacted with the film had it been gallium monochloride. It is probable that the brown film was produced by a slight reaction of hot gallium or gallium dichloride with the glass.

Vapor Pressure and Apparent Molecular Weight of Gallium Dichloride.—In order to gain information concerning the molecular state of gallium dichloride and the equilibrium between the dichloride, gallium, and the trichloride, samples of the dichloride were heated in glass cells and vapor pressure and density determinations were made. The data for four runs, in which the weight of sample per cc. of cell volume was varied, are given in Table IV. In each run the pressures for several temperatures were remeasured as the cell cooled. Good checks were obtained, proving that equilibrium had been satisfactorily established. The curves obtained by plotting temperature against pressure are shown in Fig. 2. In the first two runs the liquid phase was present for all the measurements and the curves are for saturated vapor pressures. Curves 3 and 4 flatten out beyond the point where the chlorides were completely vaporized. The equilibrium vapor pressures were found to decrease with decrease in weight of sample per cc. of cell volume. The data prove that the pressure of the vapor at equilibrium with the liquid is not a function of the temperature alone, but also is dependent upon the total weight of sample per unit volume of cell, and the system is divariant.

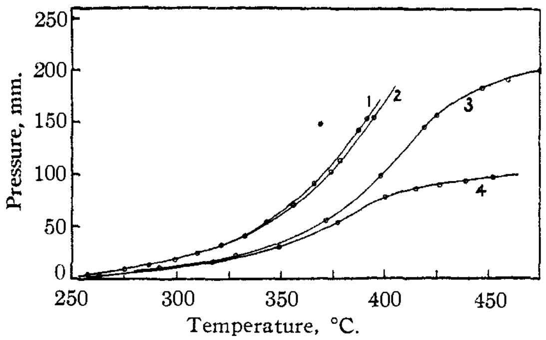

Fig. 2.—Vapor pressure of gallium dichloride.

TABLE IV

VAPOR PRESSURE AND APPARENT MOLECULAR WEIGHT OF GALLIUM DICHLORIDE

Run	Cell volume, cc.	Sample, g.	Sample per cc. cell volume, g.	Temp., °C. (±0.5)	Pressure, mm. (±0.2)	Apparent mol. wt.
1	60	0.45	0.0075	239	2.4	
				258	4.9	
				276	8.8	
				299	17.9	
				321	31.9	
				343	53.8	
				367	93.6	
				387	141.4	
				391	152.8	
				425	284.6	
				449	431.1	
2	60	0.35	.00583	223	2.0	
				245	3.9	
				264	6.7	
				287	12.9	
				310	23.6	
				332	41.4	
				356	70.2	
				374	102.6	
				379	113.0	
				394	153.9	
3	225	0.1562	.000694	222	1.3	
				288	9.0	
				328	26.2	
				372	55.8	
				398	97.6	
				419	145.1	
				425	155.2	
				447	182.0	173
				460	190.4	167
				474	200.4	161
4	225	0.0754	.000335	220	1.3	
				263	3.8	
				317	16.3	
				349	31.1	
				365	44.6	
				377	54.3	
				400	78.3	180
				416	85.3	169
				427	89.6	163
				439	93.6	159
				452	97.3	156
				465	100.6	153

Since the pressures were shown conclusively to be equilibrium values and the changes are easily reversible, the principle of the phase rule may be applied to the system. Experience with the dichloride has shown that above 200° it decomposes reversibly to gallium trichloride and gallium. Gallium trichloride in this temperature range has been shown to involve an equilibrium between the dimer and the monomer. Due to its high volatility the trichloride is probably completely in the vapor phase. Gallium is not volatile at the temperatures used and liquid gallium has been observed to exist as a separate phase in contact with liquid dichloride with no evidence of being soluble in the dichloride. Hence, in this system, when equilibrium prevails, there should be two liquid phases and one vapor phase. The system has two components and should be univariant. The authors are unable to suggest a satisfactory explanation of the observed divariancy. No reason for increasing the number of components or decreasing the number of phases can be suggested.

Molecular weights, calculated for the temperature ranges in Runs 3 and 4 where the chlorides were completely vaporized, are given in the last column in Table IV. These have been calculated on the assumption that the total weight of sample was in the vapor phase. Since some liquid gallium undoubtedly was present, the actual average molecular weights for the vapor must be somewhat lower. The theoretical molecular weights for the molecules Ga_2Cl_6, $GaCl_3$, Ga_2Cl_4, and $GaCl_2$ are 352.2, 176.1, 281.2, and 140.6, respectively. The molecular weights in Table IV can be accounted for by postulating that the vapor was a mixture of molecules of $GaCl_2$ with heavier molecules, undoubtedly Ga_2Cl_6 and $GaCl_3$ and perhaps Ga_2Cl_4.

Klemm and Tilk found that solid gallium dichloride is diamagnetic and concluded that the solid is composed of Ga_2Cl_4 molecules and not $GaCl_2$. The present investigation indicates that considerable quantities of $GaCl_2$ molecules exist in the vapor above 400° under the conditions of the experiments. There seems to be no chance of determining the configuration of the gallium dichloride molecules by an electron diffraction study of its vapor because of the complex mixture of molecules present.

Summary

1. The equilibrium vapor pressures of gallium trichloride have been studied from 50 to 200° and its thermal properties have been determined. Vapor density studies from 117 to 498° give no evidence for association beyond the dimer. The saturated vapor is more than 98.5% dimeric up to 200°, and above this temperature reversible dissociation to the monomer becomes marked, the vapor being 88% dissociated at 498°.

2. Gallium dichloride has been prepared and a method for purifying it has been devised. The properties of the pure compound have been examined. Decomposition to gallium trichloride and gallium becomes appreciable at 200°. Vapor pressure measurements from 219 to 459° indicate that the system is divariant, although it apparently involves three phases and two components. Vapor density measurements in the range 400 to 470° indicate that the vapor contains some $GaCl_2$ molecules, in which gallium must show the anomalous valence of two.

3. No evidence for the existence of gallium monochloride was observed.

ITHACA, N. Y. RECEIVED APRIL 6, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 760]

A Theory of Chromatography

BY J. NORTON WILSON

The so-called chromatographic adsorption method of analysis was originated by the Russian botanist M. Tswett.[1] He discovered that if a solution containing a mixture of colored solutes is allowed to run through a vertical glass tube filled with a suitable powdered adsorbing material, the material adsorbed in the column appears as a series of colored bands, indicating that a partial separation of the components of the solution has taken place. This series of colored bands is known as a chromatogram. The separation can be completed by a procedure known as development of the chromatogram: there is poured through the column a suitable solvent which washes the colored bands down the tube at different rates, the lowest-lying band moving the fastest. If this process is carried out in a sufficiently long tube with the use of a sufficiently large volume of solvent it is possible to effect complete separation of the original components of the solution into a series of discrete bands separated by clear spaces of adsorbent.

The technique just outlined has become in recent years an important method for the separation, purification and identification of small amounts of complex naturally-occurring organic compounds; these developments have been described at length by Zechmeister and Cholnoky.[2] The method also has been applied to some extent in inorganic chemistry[3]; the most spectacular application in this field has been to the separation of lithium isotopes.[4]

Although the nature of the phenomenon seems to be roughly understood,[2] there has appeared so

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(1) M. Tswett, *Ber. deut. botan. Ges.*, **24**, 234, 316, 384 (1906); *Ber.*, **41**, 1352 (1908); **43**, 3199 (1910); **44**, 1124 (1911).

(2) Zechmeister and Cholnoky, "Die chromatographische Adsorptionsmethode." Springer, Vienna, 1938; see also P. M. Jensen, "Die Bedeutung der chromatographischen Adsorptionsanalyse usw.," Dissertation, Technische Hochschule, Zurich, 1936; Zechmeister and Cholnoky, *Monatsh.*, **68**, 68–80 (1936).

(3) G. M. Schwab and co-workers, *Naturwiss.*, **25**, 44 (1937); *Angew. Chem.*, **50**, 546 (1937).

(4) T. I. Taylor and H. C. Urey, *J. Chem. Phys.*, **6**, 429 (1938).