

## Gaseous Complexes between Dichlorides and Trichlorides of Aluminium and Iron

BOTH aluminium chloride and ferric chloride form volatile complexes with sodium chloride<sup>1-3</sup>. It has now been found that in general they form similar complexes with dichlorides.

Vapours of  $AlCl_3$  or  $FeCl_3$  were passed over the dichlorides in 'Pyrex' or 'Vycor' tubes and the condensates analysed. The apparent vapour pressures of the dichlorides were much greater than their normal vapour pressures; some typical results for 1 atm. total pressure are given in Table 1.

Table 1. ENHANCED VOLATILITY OF DICHLORIDES IN THE PRESENCE OF TRICHLORIDES

Trichloride	Temp. (°C)	Dichloride	State	Apparent V.P. (torr)	Normal V.P. (torr) <sup>4,5</sup>
$AlCl_3$	650	$CaCl_2$	Solid	23	$2 \times 10^{-6}$
"	660	$MgCl_2$	"	85	0.07
"	600	$MnCl_2$	"	87	0.05
"	600	$CoCl_2$	"	112	0.13
"	600	$PbCl_2$	Liquid	33	4
$FeCl_3$	600	$MnCl_2$	Solid	38	0.05
"	600	$CoCl_2$	"	66	0.13
"	600	$PbCl_2$	Liquid	13	4

Despite the range of normal vapour pressures of the dichlorides, the apparent vapour pressures of the complexes vary comparatively little.

An investigation of the apparent pressures of the dichlorides as functions of the pressure of the trichlorides shows that complexes containing two trichloride molecules (presumably of the type  $CaAl_2Cl_6$ ) exist, and that in the  $AlCl_3$  systems, but not the  $FeCl_3$  systems, more complex species containing three trichloride molecules are also present.

The existence of these complexes governs the behaviour of calcium chloride and magnesium chloride when they are introduced as impurities into aluminium monochloride refining circuits (where aluminium chloride is passed over impure metallic aluminium at elevated temperatures). It also offers new methods of extracting divalent metals from ores by simultaneous chlorination and distillation of the resulting dichlorides in a stream of aluminium chloride or ferric chloride.

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<sup>1</sup> Dewing, E. W., *J. Amer. Chem. Soc.*, **77**, 2639 (1955).

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<sup>3</sup> Richards, R. R., and Gregory, N. W., *J. Phys. Chem.*, **68**, 3089 (1964).

<sup>4</sup> Kubaschewski, O., and Evans, E. L., *Metallurgical Thermochemistry* (Pergamon Press, London, 1956).

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## BIOCHEMISTRY

### The "Pink Spot" in Schizophrenia

THE discussion about "pink spot", its relation to schizophrenia and the identity of the substance(s) giving the typical reaction is still going on<sup>1-3</sup>. Because of the theoretical and practical importance of the problem we want to report briefly our observations on a series of ninety-six urine samples from patients, mainly women, with various mental diseases at the Neevengården Sykehus, Bergen, Norway. The diagnoses are in accordance with the official list used in Norway and were made solely on the basis of the patients' clinical condition. Forty-six of the cases were classified as schizophrenia, while fifty patients suffered from other mental diseases. The urines were brought to the Department of Clinical Biochemistry, Haukeland

Table 1

Drug treatment	Schizophrenia	Reaction with ninhydrin	Other mental diseases	Reaction with ninhydrin	Total number of cases
Chlorpromazine	13	Purple	14	Purple	27
Chlorprothixene ('Truxal')	5	Blue	7	Blue	12
I.Z. 914			6	Green	6
Thioridazine ('Melleril')	10	Blue fluorescence	10	Blue fluorescence	20
Other drugs	5	None	6	None	11
	4	Purple	1	Purple	2
No drugs	8	None	5	None	13
	1	Purple	1	Purple	5

Sykehus, where they were analysed, without knowledge of the diagnosis, using the original method described by Friedhoff and van Winkle<sup>4</sup>. In Table 1 the colours of the spots after staining with ninhydrin and with  $R_F$  values near that given by Friedhoff and van Winkle<sup>5</sup> are listed according to the drugs administered to the patients. It is easy to see that there is a very close correlation between the nature of the spot and the drug administered. There are, indeed, only a few exceptions in which either no spot was found in the expected position or a "pink spot" was found in patients not under treatment.

Spots with  $R_F$  values of 0.57-0.67 (mean 0.62) in the butanol:acetic acid:water (4:1:1) system used by Friedhoff and van Winkle<sup>5</sup>, staining purple with ninhydrin and turning pink with Ehrlich reagent, are seen in patients receiving chlorpromazine or closely related drugs and in only a few cases receiving other drugs or no treatment. Unlike 3,4-dimethoxyphenylethylamine (DMPE), which reacts with Ehrlich reagent only after treatment with ninhydrin, all these spots can be developed directly with Ehrlich reagent. The substance (probably 10-(3-aminopropyl)-2-chloro-5-oxo-phenothiazine (nor-2-chlorpromazine sulphoxide)<sup>6,7</sup>) also moves differently when chromatographed in a system of isopropanol:ammonia:water (20:1:2), although it behaves like DMPE in the two systems used by Friedhoff and van Winkle<sup>5</sup>. Several Ehrlich-positive, ninhydrin-negative, spots are found on thin-layer chromatograms. One of these spots was tentatively identified as chlorpromazine sulphoxide by comparison with an authentic sample. We have not yet tried to differentiate by the methods devised by Boulton and Felton<sup>2</sup> and by Bell and Somerville<sup>3</sup> between false "pink spots" and true "pink spots" that might have been present in these urines. We think it rather improbable that DMPE should be a metabolite present in easily detectable quantities. Our investigations so far seem to show quite clearly that the presence and nature of the spot(s) observed depend on the type of psychotropic drug administered rather than on the type of disease displayed by the patient.

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