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ADSORPTION OF HALOGENS ON METAL FILMS—II

ADSORPTION MEASUREMENTS AND SURFACE POTENTIALS FOR Cl_2 AND $TiCl_4$ ON TITANIUM AND SOME OTHER METALS

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Abstract—The adsorption of chlorine on titanium was extremely rapid up to about monolayer coverage both at 295°K and 151°K but for pressures $> 10^{-5}$ mm Hg adsorption exceeded monolayer coverage and a slow uptake of gas was found. On aluminium at 295°K chlorine sorption proceeded readily to coverages in excess of fourteen monolayers with pressures $< 7 \times 10^{-5}$ mm Hg. On platinum at 295°K chlorine adsorption reached a limiting value of about two monolayers at $0{\cdot}5 \times 10^{-3}$ mm Hg and no slow process was observed. Monolayer uptakes to be expected for regular and for random arrays of adatoms have been calculated and the experimental monolayer adsorptions show reasonable agreement with the calculated values. At low coverages ($0 < \theta < 0{\cdot}1$) positive surface potentials for the adsorption of chlorine on titanium were observed and it is suggested that this was due to partial burial of the adatom in the metal surface. At higher coverages the surface potential became negative, the maximum excursion being $-2{\cdot}1$ V. At 277°K titanium tetrachloride chemisorbed on titanium and the magnitude of the observed surface potential together with a comparison of experimental and calculated monolayer capacities suggests dissociative adsorption, probably to $Cl + TiCl_3$ residues on the surface as the initial step. No titanium tetrachloride adsorption could be detected on platinum at 277°K or 453°K, but adsorption occurred readily on nickel at 277°K. A mechanism is suggested for the production of titanium tetrachloride from chlorine and titanium.

1. INTRODUCTION

A PREVIOUS paper⁽¹⁾—subsequently referred to as I—described the interaction between chlorine and nickel. It was established that at 293°K and 151°K adsorption was initially unactivated but that dissociative adsorption of molecular chlorine in excess of about two monolayers occurred by a slow process. At low coverages ($\theta < 0{\cdot}1$) positive surface potentials were found which were attributed to the partial burial of adsorbed chlorine in the metal surface. At higher coverages surface potentials became negative.

The present paper describes the extension of this work to the adsorption of chlorine on evaporated films of titanium, platinum and aluminium and to the adsorption of titanium tetrachloride on these metals and on evaporated nickel. The adsorption of titanium tetrachloride was of interest since dissociative adsorption would lead to the formation of a titanium-metal bond; furthermore, with titanium it was of interest to compare the result of the adsorption of titanium tetrachloride with that of chlorine since it was thought possible that both processes could lead to similar surface products.

The only previous surface potential measurements for chlorine on titanium are those measured photoelectrically by MALMUD and KRUMBEIN.⁽²⁾

2. EXPERIMENTAL

The general apparatus, vacuum technique, details of gas manipulation and of surface potential measurement (by the diode method) have been previously described in I.*

In the examination of the electrical resistance of

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* Filament temperatures quoted in Part I should read °K.

thin titanium films, resistances were measured with a shunted Wheatstone bridge. Measured resistances were about 50 Ω and measurements were reproducible to ± 0·005 Ω. For this purpose the reaction vessel was immersed in oil in a large vacuum flask to maintain constant temperature.

Titanium tetrachloride was purified by repeated fractional distillation over copper filings until filings remained bright, collecting the fraction boiling at 409°K. The final sample was vacuum distilled into the storage vessel on the vacuum line. Since titanium tetrachloride reacts fairly rapidly with "Florube"* grease no greased joints or taps were used in the titanium tetrachloride purification line: where necessary all-metal taps (HOKE, A434) were used. Vapour pressures in the titanium tetrachloride reservoir were calculated by the relationship found by WEED,(3)

$$\log_e p(\text{mm Hg}) = 59{\cdot}3594 - \frac{7696{\cdot}935}{T(^\circ\text{K})} - 5{\cdot}340177 \log_e T + 2{\cdot}327 \times 10^{-4}\, T$$

valid for solid titanium tetrachloride in the range 200–249°K. The temperature of the titanium tetrachloride reservoir was controlled to about 228°K using a slurry bath of molten monochlorbenzene.

Adsorption measurements with titanium tetrachloride had to be corrected for adsorption on the exposed glass and this was done in a manner similar to that described for chlorine in Part I.

Titanium films were deposited onto the walls of the adsorption cell maintained at 273°K by direct evaporation from 0·22 mm diameter wire at 1·95 A for about 20 min after outgassing for 3 hr at 1·2 A. This outgassing temperature is in excess of the α–β phase transition temperature (1157°K). Titanium wire was of purity in excess of 99·9 per cent. An electron diffraction examination of a film specimen showed it to have the same crystal structure (hexagonal close-packed) and, to within two per cent, the same lattice parameters as bulk titanium. The titanium film showed some preferred orientation with the $(11\bar{2}0)$ plane parallel to the glass backing.

Platinum films were prepared by the technique described by KEMBALL(4) from Johnson and Matthey spectroscopically standardized wire.

Aluminium films were prepared from chips of Johnson and Matthey spectroscopically standardized metal in a helical coil wound from 0·5 mm diameter tungsten. The first film was discarded after the aluminium had wetted the tungsten and evaporation was effected at 9·5 A after outgassing at 6·5 A for 3 hr.

For surface area estimation xenon and oxygen isotherms were measured on titanium films in a separate series of experiments using a conventional vacuum line. Such films were prepared under identical conditions to those employed for halogen adsorption. During measurements with xenon mercury vapour was trapped at 195°K.

3. RESULTS AND DISCUSSION

(i) *Xenon and oxygen adsorption on titanium*

Xenon adsorption isotherms were measured at 90°K over the range $0 < p/p_0 < 0{\cdot}02$. Thermomolecular flow corrections throughout this paper were made using formulae due to PORTER.(5) Over this range the isotherm data accurately followed B.E.T. plots(6) from which film areas were obtained using p_0 for solid xenon at 90°K of $6{\cdot}3 \times 10^{-2}$ mm Hg and assuming an effective area per adsorbed xenon of 24·6 Å^2. This latter figure was obtained on the assumption that in the surface the three densest planes—(0001), $(10\bar{1}0)$, $(11\bar{2}0)$—were equally exposed and that xenon atoms were adsorbed over crystallographic surface sites giving a lattice-packed monolayer. The validity of the assumption of lattice packing of adsorbed xenon in relation to surface area measurement has been discussed by ANDERSON and BAKER.(7)

An attempt to use hydrogen adsorption at 90°K for surface area estimation failed because of the continued slow uptake of gas.

Oxygen adsorption measurements at 90°K were made for comparison with B.E.T. areas in order to provide a method for the measurement of surface areas for light titanium films the areas of which were too small for satisfactory measurement by xenon adsorption. At each point oxygen adsorption equilibrium was reached in less than 5 min and isotherms were substantially horizontal above 5×10^{-4} mm Hg so that the characteristic rapid oxygen uptake was taken at about 10^{-3} mm Hg.

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* Fluorcarbon grease, "Florube" grease A; Imperial Chemical Industries.

Xenon and oxygen adsorption results on a number of titanium films are collected into Fig. 1 from which it follows that at 90°K rapid oxygen adsorption proceeds to the extent of $2{\cdot}44 \times 10^{15}$ mol cm^{-2}. The comparatively small size of oxygen makes the identification of crystallographic adsorption sites on all except the close-packed (0001) plane very uncertain and we therefore adopt for the average number of oxygen adsorption sites $0{\cdot}97 \times 10^{15}$ sites cm^{-2} proposed by Zweitering, Koks and van Heerden.(8) On this basis, this extent of adsorption of oxygen corresponds to 5·0 monolayers. This is to be compared with the adsorption of oxygen at 295°K on titanium films measured by Brennan, Hayward and Trapnell(9) when, using the above value for the density of sites, rapid oxygen uptake proceeded to about 9·7 monolayers. By combining these data we may compute a critical temperature (T_c) above which growth of an oxide layer on titanium ceases to be restricted to a limiting thickness. Using the relation deduced by Grimley and Trapnell(10) the computed value for T_c is about 530°K which is in agreement with the finding by Gulbransen and Andrew(11) of parabolic growth above 523°K.

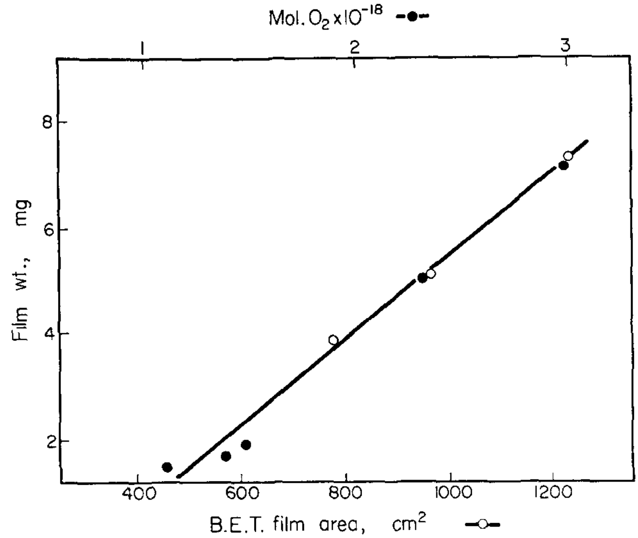

Fig. 1. B.E.T. (xenon) area and rapid oxygen adsorption (90°K) vs. weight of titanium films.

The data in Fig. 1 show in the range 2–8 mg the ratio film area/film weight is approximately constant and equal to 182 cm^2 mg^{-1} and this figure was used to calculate surface areas of films used in halogen adsorption experiments.

(ii) *Adsorption of chlorine*

The convention will be adopted that n_{Cl_2} refers to the equivalent number of adsorbed chlorine molecules per cm^2. Unless otherwise stated pressures were measured about 5 min after admitting the chlorine dose to the film. Isotherms were measured on the three metals mainly to establish their relative behaviour and reactivity towards chlorine in the low pressure region. Fig. 2 shows an adsorption isotherm at 295°K containing data from two titanium films—5·3 mg, area 960 cm^2 and 6·3 mg, area 1100 cm^2. For all pressures up to about 10^{-5} mm Hg equilibrium was attained rapidly; however the two points above 6×10^{-4} mm Hg are not equilibrium values and the attached arrows indicate the general trend of a slow movement towards equilibrium. After the completion of the isotherm at 295°K a search was made for the presence of titanium tetrachloride by freezing down a small side-arm at 151°K—when the vapour pressure of titanium tetrachloride was estimated at ~ 10^{-8} mm Hg. After pumping away the residual chlorine, no pressure increase due to titanium tetrachloride ($< 10^{-5}$ mm Hg) was detected on warming the side-arm to room temperature, nor was any detected in a similar manner after flooding the film to about 10^{-1} mm Hg with chlorine at 295°K for 5 min. However, heating a titanium film to about 600°K in chlorine initially at 1×10^{-3} mm Hg returned titanium tetrachloride to the gas phase at about 2×10^{-4} mm Hg. At 400°K considerable production of titanium tetrachloride occurred when a 4·0 mg film was about half converted to titanium tetrachloride in 10 min with chlorine at about 1 mm Hg. Because of the ready production of titanium tetrachloride, no systematic adsorption measurements were attempted above 295°K. At 151°K on a 5·6 mg titanium film, the initial chlorine uptake was still found to be immeasurably fast.

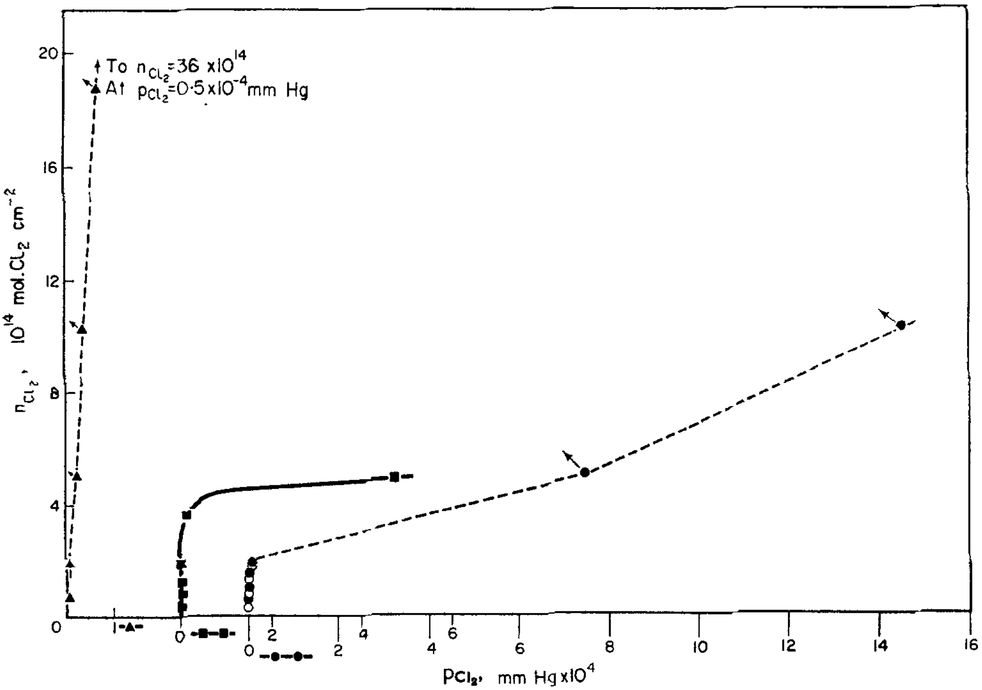

FIG. 2. Adsorption of chlorine at 295°K.

titanium: ●, 5·3 mg; ○, 6·3 mg film.
platinum: ■, 6·9 mg film.
aluminium: ▲, 3·0 mg film.

Adsorption measurements at 293°K on films of platinum (6·9 mg) and aluminium (3·0 mg) are also shown in Fig. 2. While all of the points for platinum were apparently at equilibrium, those for aluminium were moving slowly to lower pressures and the positions of these points are thus only approximate. Flooding the aluminium film at 293°K with chlorine to about 10^{-1} mm Hg rapidly caused it to lose its metallic appearance and electrical conductance presumably by conversion to aluminium chloride.

From Fig. 2, the value of n_{Cl_2} for titanium for which a measurable ($> 10^{-6}$ mm Hg) equilibrium chlorine pressure was first observed is about $1 \cdot 8 \times 10^{14}$ mol cm^{-2}. If it is assumed that chlorine is dissociatively adsorbed at surface crystallographic positions such that contact is made with the maximum number of surface titanium atoms, the most closely packed regular arrays of occupied

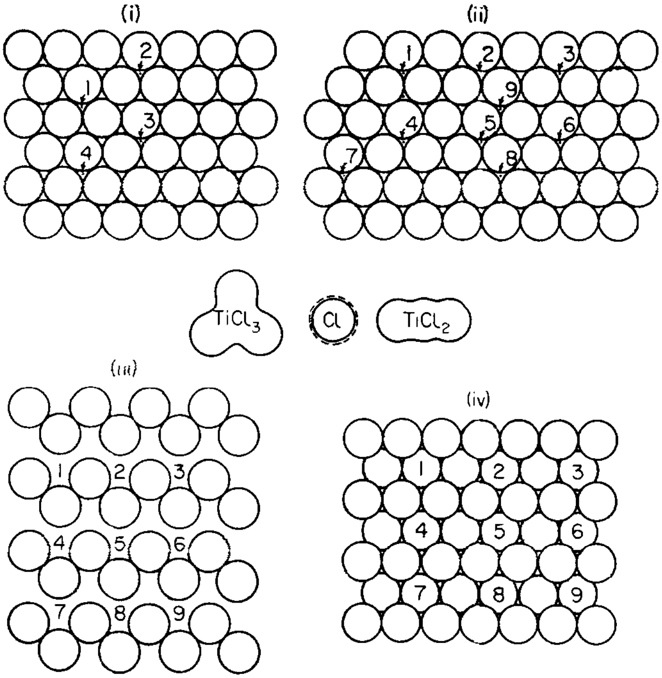

FIG. 3. Adsorption in regular arrays on surface crystallographic sites of titanium. Estimated van der Waals dimensions of the $TiCl_3$, $TiCl_2$ and Cl residues shown to scale: the broken outline is for a chloride ion.

(i) (0001) face: Cl_2 as 2 Cl; sites 1–4 Cl. $TiCl_4$ as TiCl+3 Cl; site 1 TiCl, sites 2,3,4 Cl.

(ii) (0001) face: $TiCl_4$ as $TiCl_3$+Cl; sites 1,3,5 $TiCl_3$, sites 2,4,6Cl, sites 7,8,9 vacant. $TiCl_4$ as $TiCl_2$+2 Cl; sites 1,3,7,8 $TiCl_2$ sites 4,9 Cl, sites 2,5,6 vacant.

(iii) $(11\bar{2}0)$ face: Cl_2 as 2 Cl; sites 1–9 Cl. $TiCl_4$ as $TiCl_3$+Cl; sites 2,4,6,8 $TiCl_3$, sites 1,3,5,7,9 Cl. $TiCl_4$ as $TiCl_2$+2 Cl; sites 1,3,7,9 $TiCl_2$, sites 2,4,6,8 Cl, site 5 vacant. $TiCl_4$ as TiCl+3 Cl; sites 1,3,7,9 TiCl, sites 2,4,5,6,8 Cl.

(iv) $(10\bar{1}0)$ face: Cl_2 as 2 Cl; sites 1–9 Cl. $TiCl_4$ as $TiCl_3$+Cl; sites 1,3,5,7,9 $TiCl_3$, sites 2,4,6,8 Cl. $TiCl_4$ as $TiCl_2$+2 Cl; sites 1,3,7,9 $TiCl_2$, sites 2,4,6,8 Cl, site 5 vacant. $TiCl_4$ as TiCl+3 Cl; sites 1,3,7,9 TiCl, sites 2,4,5,6,8 Cl.

sites on the (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ planes may be generated by extending the arrays shown in Fig. 3. The diameter of Cl^- is 3·62 Å while the effective van der Waals diameter of covalently bonded chlorine (ambiguously referred to in I as the covalent diameter) is about 3·2 Å; both of these values are sufficiently large that adsorption either as an ion or a covalently bound atom on a site on the (0001) and $(10\bar{1}0)$ faces of titanium will exclude adsorption on nearest neighbour sites. However, completely regular arrays of adatoms cannot be formed if adsorption is both dissociative and immobile. For this model, computed monolayer adsorptions have been obtained for the (0001) and $(10\bar{1}0)$ planes by a Monte Carlo calculation, filling an array of 1000 numbered adsorption sites in a random fashion by using a table of random numbers: on the $(11\bar{2}0)$ plane nearest neighbour exclusion does not occur and for the approximately square array of sites we have adopted the

Table 1. *Calculated monolayer coverages for chlorine on titanium*

Plane	Regular monolayer		Random monolayer	
	Percentage of sites occupied	n_{Cl_2} (10^{14} mol cm^{-2})	Percentage of sites occupied	n_{Cl_2} (10^{14} mol cm^{-2})
(0001)	33·3	2·24	23	1·55
(10$\bar{1}$0)	50	1·83	40	1·47
(11$\bar{2}$0)	100	2·06	92	1·90
Mean		2·04		1·64

value of ninety-two per cent occupation calculated by ROBERTS(10) for an exactly square array. No great accuracy is claimed for the calculations, although repeat calculations indicate an error of not more than about five per cent. In the calculations for the (0001) and (10$\bar{1}$0) planes it was assumed that dissociative adsorption placed adatoms only on pairs of sites separated by the minimum allowed distance. Values of n_{Cl_2} for monolayer coverage ($\theta = 1$) for the "regular" and "random" models are listed in Table 1: the mean values of n_{Cl_2} have been obtained on the assumption that the three planes are equally exposed. The experimental monolayer adsorption, $1{\cdot}8 \times 10^{14}$ mol cm^{-2} (*vide supra*), is bracketed by the computed values—$2{\cdot}04 \times 10^{14}$ mol cm^{-2} (regular) and $1{\cdot}64 \times 10^{14}$ mol cm^{-2} (random)—and the agreement is probably as good as could be expected. In subsequent discussions for the titanium/chlorine system monolayer adsorption will be taken as $n_{\mathrm{Cl}_2} = 1{\cdot}8 \times 10^{14}$ mol cm^{-2}.

For the 6·9 mg platinum film the area was estimated to be 780 cm^2 from the area/weight relationship established by ANDERSON and BAKER(7) using B.E.T. xenon measurements. The area of the 3 mg aluminium film was estimated to be about 110 cm^2 from the area/weight relationship obtained by ELEY and WILKINSON.(12) Both platinum and aluminium have face-centred cubic structures and, as on nickel, adsorption will be sterically excluded on nearest neighbour sites, the regular array of adatoms on the (111) plane resembling that on the (0001) plane of titanium while on the (100) and (110) planes we refer to I. The degree of occupation of (111), (100) and (110) planes obtained by Monte Carlo calculations assuming nearest neighbour exclusion and dissociative immobile adsorption are given in Table 2.* The figure for the (100) plane is in reasonable agreement with ROBERT's(13) estimate of about thirty seven per cent.

On the assumption that the three planes appear equally in the film, the computed average monolayer values of n_{Cl_2} for platinum and aluminium

Table 2. *Degree of occupation of surface planes*

		Percentage of sites occupied	
		Regular monolayer	Random monolayer
F.C.C.	(111)	33·3	23
	(100)	50	35
	(110)	50	40

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* As a check on the accuracy, the Monte Carlo calculation for the (110) plane was also performed as an experiment on the computer C.S.I.R.A.C. and this gave as the result of filling 31,000 sites a degree of occupation of 40·5 per cent with 95 per cent confidence limits of ± 0·2 per cent.

are respectively—regular, $2{\cdot}58 \times 10^{14}$ and $2{\cdot}44 \times 10^{14}$ mol cm^{-2}; random, $1{\cdot}9 \times 10^{14}$ and $1{\cdot}8 \times 10^{14}$ mol cm^{-2}. In subsequent discussion, for monolayer adsorption on these metals the approximate value of $2{\cdot}0 \times 10^{14}$ mol cm^{-2} is used.

In Fig. 4 are recorded values for the surface potential (S_{Cl_2}) for the titanium/chlorine system for two films at 295°K and for one film each at 151°K and 358°K. The values of S correspond to measurements taken approximately 15 min after the introduction of each dose of gas and were constant to within 0·1 V over a further 10 min. A positive S is taken to correspond to a work function reduction. It was found that a film, on which chlorine had been adsorbed at 295°K to about 5 M* and for which the value of S_{Cl_2} was $-2{\cdot}1$ V, on heating at 600°K for 10 min in chlorine, initially at 10^{-3} mm Hg, followed by pumping and then cooling to room temperature, yielded a value of S_{Cl_2} of $-1{\cdot}1$ V.

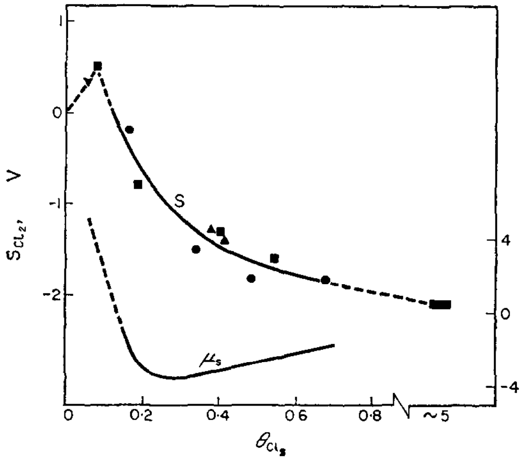

FIG. 4. Dependence of surface potential (S_{Cl_2}) and surface dipole moment (μ_s) on surface coverage (θ_{Cl_2}) for chlorine on titanium. Monolayer coverage taken as $n_{Cl_2} = 1{\cdot}8 \times 10^{14}$ mol. Cl$_2$ cm^{-2}.

■, 4·3 mg film at 295°K
●, 6·3 mg film at 295°K
▲, 5·6 mg film at 151°K
▼, 4·0 mg film at 358°K

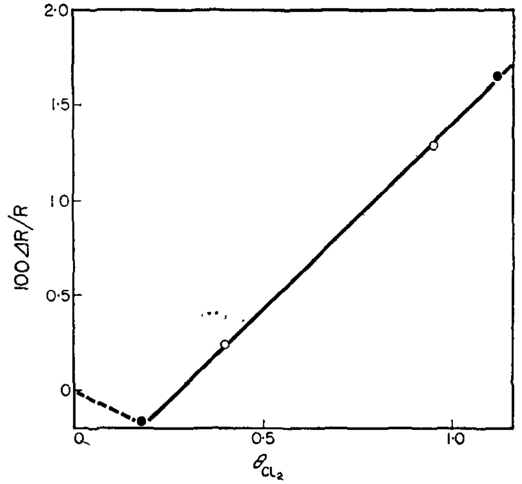

FIG. 5. Relative resistance change for thin titanium film vs. surface coverage (θ_{Cl_2}) of chlorine at 295°K. Monolayer coverage taken as $n_{Cl_2} = 1{\cdot}8 \times 10^{14}$ mol. Cl$_2$ cm^{-2}

○, 1·3 mg film
●, 1·8 mg film

Surface potentials for the platinum/chlorine and aluminium/chlorine systems were examined much less extensively than with titanium and the data are collected into Table 3. Because of the low area of the aluminium film values for the surface coverage are only semiquantitative.

Table 3. Surface potentials for the adsorption of chlorine on platinum and aluminium at 295°K

Metal	θ_{Cl_2}	S_{Cl_2}, V
Platinum	0·5	−0·1
	0·9	−0·5
Aluminium	Approx. 0·3 and 0·8	~ −0·1

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* For convenience the notation M refers to monolayer adsorption.

Using two thin titanium films of weights 1·3 and 1·8 mg, the change in film resistance with chlorine adsorption at 295°K was measured for the region $\theta_{\mathrm{Cl}_2} \lesssim 1$. The films were deposited at 273°K and, prior to chlorine admission, maintained at 295°K until constant resistance was achieved, a period of about 100 min being required. The relative change in resistance is shown as a function of coverage in Fig. 5. The initial drop in resistance which is attributed to chemisorption sintering is followed by a rise in which the relative resistance change is linearly dependent on coverage. At $\theta_{\mathrm{Cl}_2} = 1$ the value of $\Delta R/R$, 0·014, is of the same order as the ratio of the number of adsorbed chlorine atoms to the total number of titanium atoms in the film, ~ 0·01.

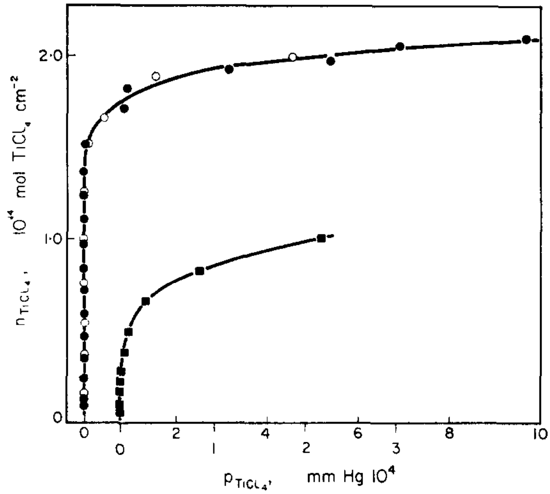


FIG. 6. Adsorption of titanium tetrachloride at 277°K titanium: ●, 6·0 mg; ○, 5·0 mg film. nickel: ■, 5·2 mg film.

(iii) *Adsorption of titanium tetrachloride*

In Fig. 6 is plotted a combined isotherm for the adsorption of titanium tetrachloride at 277°K on two titanium films, (a) 6·0 mg (area 1090 cm^2), (b) 5·0 mg (area 910 cm^2). At all points equilibrium was attained rapidly and no slow process was observed. Relevant surface potential data are given in Table 4. Surface potential measurements were only made when the pressure of titanium tetrachloride was $< 10^{-6}$ mm Hg. For comparison, less extensive measurements were made on films of nickel, 5·2 mg, area 400 cm^2; platinum, 8·1 mg, area 920 cm^2 and aluminium, 2·8 mg, area ~ 110 cm^2. The data for nickel are also collected into Fig. 6 and Table 4. When, in the adsorption of titanium tetrachloride on titanium, an equilibrium pressure of about 10^{-3} mm Hg had been reached, the gas phase was examined for the presence of chlorine by freezing down at 151°K. The residual pressure was $< 10^{-6}$ mm Hg indicating both the absence of chlorine and residual contaminant. It was found that running the diode filament in titanium tetrachloride at 10^{-3} mm Hg in the presence of a titanium film had no effect on the pressure or on the surface potential, although with chlorine under comparable conditions further adsorption was rapid (cf. I).

The magnitude of the surface potentials generated by the adsorption of titanium tetrachloride on titanium and the very low ($< 10^{-6}$ mm Hg) equilibrium pressures found over the major part of the coverage range suggest that the titanium tetrachloride is chemisorbed under these conditions. On the assumption that dissociative chemisorption occurs to yield (i) TiCl_3 and Cl, (ii) TiCl_2 and 2Cl, and (iii) TiCl and 3Cl, the regular array with closest allowed packing on the

Table 4. Surface potentials for the adsorption of titanium tetrachloride on titanium and nickel at 277°K

Metal	n_{TiCl_4} 10^{14} mol TiCl_4 cm^{-2}	S_{TiCl_4}, V
Titanium	0·16	$-0{\cdot}2_2$
	0·76	$-0{\cdot}8_6$
Nickel	0·17	$-0{\cdot}3_4$
	0·31	$-0{\cdot}6_1$

(0001), (10$\bar{1}$0) and (11$\bar{2}$0) surface planes of titanium may be generated by extending the arrays shown in Fig. 3. As before, it is assumed that the adsorption sites are normal crystallographic positions. The assumption is made that the $TiCl_3$, $TiCl_2$ and TiCl groups would be bonded to the surface by the titanium atom. The effective (van der Waals) size of these chemisorbed groups has been estimated on the assumption that bond angles and bond lengths are the same as in titanium tetrachloride(14) and that the van der Waals diameter of each Cl is the same as for Cl in molecular chlorine (taken as 3·2 Å). On this basis the effective areas per adsorbed titanium tetrachloride at $\theta_{\mathrm{TiCl}_4} = 1$ on titanium are

	Dissociation to	
	$TiCl_3+Cl$	$TiCl_2+2Cl$ or $TiCl+3Cl$
(0001)	59·5 Å^2	89·2 Å^2
(10$\bar{1}$0)	54·6 Å^2	109·2 Å^2
(11$\bar{2}$0)	48·4 Å^2	96·8 Å^2

leading to expected average values for n_{TiCl_4} at $\theta_{\mathrm{TiCl}_4} = 1$ of $1{\cdot}84\times10^{14}$ mol cm^{-2} for dissociation to $TiCl_3$ and Cl and $1{\cdot}02\times10^{14}$ mol cm^{-2} for dissociation to TiCl and 2Cl or TiCl and 3Cl.

For the dissociative adsorption of titanium tetrachloride on nickel the values of n_{TiCl_4} at $\theta_{\mathrm{TiCl}_4} = 1$, averaged over the planes (111), (100), (110) are $1{\cdot}81\times10^{14}$ mol cm^{-2}, $1{\cdot}55\times10^{14}$ mol cm^{-2} and $1{\cdot}61\times10^{14}$ mol cm^{-2} for dissociation to $TiCl_3$ and Cl, $TiCl_2$ and 2Cl and to TiCl and 3Cl respectively: these values were computed in a manner analogous to that used for titanium assuming closest permitted packing in regular arrays. Because of the possible complexity of the packing, Monte Carlo computations were not attempted for any system with titanium tetrachloride. However, the figures for the regular monolayers are upper limits and, making a rough estimate by comparison with the chlorine case, we may anticipate monolayer adsorption for random packing to be lower by about twenty to thirty per cent. Fig. 6 shows that on titanium the value of n_{TiCl_4} for which a measurable ($> 10^{-6}$ mm Hg) equilibrium pressure of titanium tetrachloride was first observed is about $1{\cdot}6\times10^{14}$ mol cm^{-2}. For subsequent discussion this value has been adopted for monolayer adsorption on both titanium and nickel. Only a small adsorption of titanium tetrachloride could be detected on aluminium at 277°K: at an equilibrium pressure of $5{\cdot}3\times10^{-5}$ mm Hg n_{TiCl_4} was approximately $0{\cdot}3\times10^{14}$ mol cm^{-2} and the surface potential measured after pumping was $-0{\cdot}9$ V. Because of the low surface area of the aluminium film the coverage value is only of semi-quantitative significance. On platinum no adsorption of titanium tetrachloride and no significant surface potential could be detected either at 277°K or at 453°K.

4. GENERAL DISCUSSION

It is seen by reference to Fig. 2 that for pressures greater than 10^{-5} mm Hg the amount of chlorine sorbed on titanium at 295°K is in excess of that required for monolayer coverage; at $1{\cdot}45\times10^{-3}$ mm Hg adsorption proceeded in excess of ~ 5 M. On aluminium at 295°K it is evident that the sorption of chlorine proceeds extremely rapidly even at coverages in excess of ~ 14 M with pressures $< 7\times10^{-5}$ mm Hg. On platinum at 295°K chlorine adsorption reaches a limiting value of ~ 2 M at about $0{\cdot}5\times10^{-3}$ mm Hg. We may note that using the data in Table 2 we compute for a random monolayer of chlorine on nickel a value for n_{Cl_2} of $2{\cdot}4\times10^{14}$ mol cm^{-2}, to be compared with $3{\cdot}3\times10^{14}$ mol cm^{-2} for a regular monolayer: these two values bracket the experimental monolayer adsorption of 3×10^{14} mol cm^{-2} (cf. I).

From these data and from I we note that the relative ease of reaction of these metals with chlorine at 10^{-4}–10^{-3} mm Hg and 295°K is $\mathrm{Al} \gg \mathrm{Ti} \gtrsim \mathrm{Ni} > \mathrm{Pt}$. It seems relevant to compare the reactivity of aluminium with titanium. For titanium the ultimate corrosion product with excess chlorine is titanium tetrachloride; however one would expect this to be formed via the precursors titanium II chloride ($TiCl_2$) and titanium III chloride ($TiCl_3$). Both of the latter are comparatively involatile. $TiCl_3$ has the same crystal structure as iron III chloride(15) and is thus probably highly polymerized: it only sublimes very slowly at 703°K.(16) $TiCl_2$ has a layer lattice CdI_2 structure(17) and remains involatile up to the temperature at which decomposition becomes appreciable—about 750°K.(16, 18) These lower chlorides are thus apparently able to form a continuous layer on the titanium surface and offer a degree of protection from further attack provided the temperature and chlorine pressure are sufficiently low. On the other hand, although solid aluminium chloride is of appreciable ionic character(16) with a layer lattice structure,(19) its low sublimation temperature (451°K at 1 atm) indicates a very weakly bonded lattice, presumably thus providing only a poor barrier for diffusion of reacting species.

The positive values of S_{Cl_2} found in the titanium/chlorine system at low θ_{Cl_2} are similar to the behaviour described for the nickel/chlorine system in I. The positive excursion with titanium at 295°K ($\sim 0{\cdot}5$ V) is rather greater than for nickel ($\sim 0{\cdot}2$ V) and the mechanism of generation is considered to be similar for both metals, that is, partial burial of the electronegative adatom in the metal surface (cf. I). With platinum and aluminium insufficient data are available to determine if similar positive excursions occur although the small magnitude of the value for aluminium (about $-0{\cdot}1$ V, cf. Table 3) may result from partial burial of a proportion of the adatoms in the surface. For platinum the surface potentials for chlorine recorded in Table 3 are rather lower than for oxygen for which a value of about $-1{\cdot}2$ V has been reported.(20) This is in qualitative agreement with the lower electronegativity(21) of chlorine (3·0) than oxygen (3·5). For titanium and nickel positive values of S_{Cl_2} are limited to the region of $0 < \theta < 0{\cdot}1$; to comment upon this comparatively narrow range of coverage we note that for initial adsorption the type of site where the interaction energy is greatest will be preferred and, further, one may well expect a sufficiently high heat of adsorption to be a prerequisite for adatom burial. For instance, examination of a molecular model suggests that, using as a criterion maximum initial co-ordination of the adatom, of the three planes discussed previously preference would be expected for a $(10\bar{1}0)$ site on titanium and a (110) site on nickel. Furthermore, Brennan, Hayward and Trapnell(8) have recently reported that, per mole of oxygen, the initial heat of adsorption on a number of metals is close to the heat of formation of a stable bulk oxide: this result is the more readily understandable if the adatom were buried in the surface to an extent that increased the number of nearest neighbour metal atoms nearer to the value characteristic of the bulk oxide.

For chlorine on titanium the magnitude of the surface dipole, μ_s (cf. Fig. 4) is, over most of the coverage range, considerably greater than on nickel (Part I). For instance at $\theta = 0{\cdot}5$ the values of μ_s are about $-2{\cdot}3$ D and $-0{\cdot}4$ D respectively. This difference is in qualitative agreement with the lower electronegativity(21) of titanium (1·5) than nickel (1·8), although a quantitative discussion of μ_s in terms of the character of the bond does not appear warranted without more precise knowledge of the geometry of the adatom at its adsorption site.

The value for S_{Cl_2} of $-2{\cdot}1$ V for a thick chloride layer (~ 5 M) on titanium is considerably different from the apparent value of $-0{\cdot}3$ V reported by Malmud and Krumbein(2) for titanium specimens which had been extensively soaked in high (10 cm Hg) chlorine pressures and which must thus certainly have been coated with chloride layers of thickness $\geqslant 5$ M. We consider that this difference arises because, for metals which become heavily coated with a surface layer of reaction product, measurement of the shift in the photoelectric threshold and measurement of the shift in the diode characteristic do not necessarily measure the same quantity. The photoelectron from the coated specimen may well come from the surface layer not the metal substrate; S so obtained will then be a measure of the difference between the work function of the virgin metal and of the layer material.

Alternatively, the direct measurement of the change in contact potential either by the diode technique or by a vibrating condenser method gives for S a measure of the change in the overall phase-boundary potential between the metal and free space. This distinction does not appear to have been sufficiently appreciated in the past. It may, for instance, account for the large apparent difference between the values of S measured for the nickel/oxygen system by Bosworth(22) (diode, $S = -1{\cdot}4$ V), Mignolet(23) (condenser, $S = -1{\cdot}6$ V) and by Klemperer and Anderson,(24) (photoelectric, $S \nless -0{\cdot}7$ V).

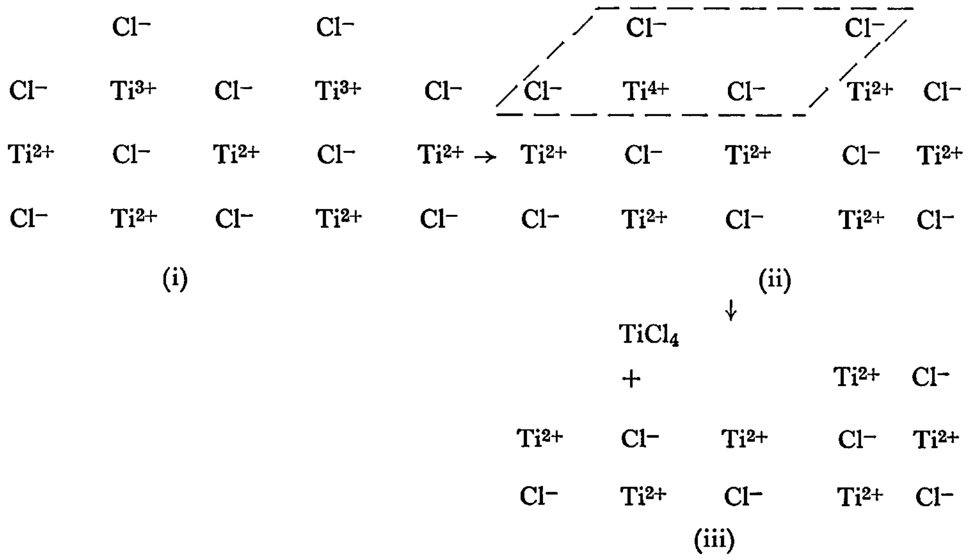
Because of the difficulty of assessing the most reasonable mode of packing of the radicals on the surface, it is not possible from the data in Fig. 6 to estimate with certainty the degree of dissociative fragmentation (i.e. the value of x for the surface residue TiCl_x) occurring with titanium tetrachloride: an examination of the data shows that on titanium adsorption at 277°K reaches a limiting value which is not more than some 1–2 times the expected monolayer capacity for dissociative adsorption. However, using the surface potential/chlorine coverage data given in Fig. 4, it is estimated that, with $n_{\mathrm{TiCl}_4} = 0{\cdot}76 \times 10^{14}$ mol cm^{-2} on titanium, adsorption as $\mathrm{TiCl}_3+\mathrm{Cl}$ would result in a contribution to S_{TiCl_4} from the dissociated chlorine atoms of $-0{\cdot}7$ V, while for adsorption as $\mathrm{TiCl}_2+2\mathrm{Cl}$ the corresponding figure is $-1{\cdot}5$ V. In as much as at this value of n_{TiCl_4} the observed S_{TiCl_4} was $-0{\cdot}8_5$ V (Table 4), these data lend support to the $\mathrm{TiCl}_3+\mathrm{Cl}$ dissociative mode, since the alternative would seem to require an improbably high positive contribution to S_{TiCl_4} from the adsorbed TiCl_2 residue.

The observed upper limit to the adsorption of titanium tetrachloride is relevant to the failure of further titanium tetrachloride adsorption to occur in the presence of a tungsten filament at 2495°K. Appreciable thermal dissociation of titanium tetrachloride seems probable under these conditions, since from (an extrapolation of) the thermodynamic data of SKINNER and RUEHRWEIN(18) the equilibrium constant at 2500°K for the dissociation of titanium tetrachloride to $\mathrm{TiCl}_3(g)$ and $\mathrm{Cl}(g)$ is estimated at about $0{\cdot}1$ atm. More extensive dissociation is less favourable. It thus seems likely that this failure was due to the inability of the surface to accommodate further TiCl_3 residues without reconversion to titanium tetrachloride, presumably by reaction with adsorbed chlorine atoms. Since chemisorption of chlorine occurs on platinum, we suggest that the failure of titanium tetrachloride to chemisorb on this metal is due to a very low energy for the Pt–(TiCl_x) bond.

The free energy data of HEAD(25) show that per mole of chlorine the formation from the elements of TiCl_2 is favoured over TiCl_3 at 295°K. We thus tentatively suggest that, particularly in very thin chloride layers (< 50 Å) where electron transfer from the substrate is relatively easy, the surface chloride layer consists of Ti^{2+} and Cl^- and that chlorine adsorption occurs upon this layer, according to

$$\mathrm{Cl}_2+2\mathrm{Ti}^{2+}_s \rightarrow 2\mathrm{Cl}^-_{\mathrm{ads}}+2\mathrm{Ti}^{3+}_s.$$

We further suggest two possible modes of destruction of the Ti^{3+}—either (a) reconversion to Ti^{2+} by electron transfer, together with the migration of titanium from the substrate to build $\mathrm{Cl}^-_{\mathrm{ads}}$ into the regular lattice of the surface layer or (b) if the surface layer has grown to a thickness that the Ti^{3+} have a sufficient lifetime, the formation and elimination of titanium tetrachloride according to the following scheme (the representation is schematic and does not show overall charge neutrality):



The observed change in S_{Cl_2} from $-2{\cdot}1$ V to $-1{\cdot}1$ V (*vide supra*) consequent upon the formation of some $TiCl_4$ by heating to 600°K in 10^{-3} mm Hg of chlorine agrees with this proposed scheme since a change in S_{Cl_2} in this direction would be expected on the removal of adsorbed chlorine.

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