

The mechanism of the adsorption of gold cyanide on activated carbon

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SYNOPSIS

X-ray photoelectron spectroscopy showed that the adsorption of gold cyanide on carbon in the presence or absence of electrolytes and acids proceeds by the same mechanism. Although the identity of the gold cyanide adsorbate is not known, the mechanism appears to have an initial adsorption stage that involves the adsorption of an ion pair: $M^{n+}[Au(CN)_2]_n^-$, where M^{n+} is a metal ion (for example Na^+ , K^+ and Ca^{2+}) that has a lower solubility than the $Au(CN)_2^-$ anion in the adsorption medium, followed by a reduction step in which either a sub-stoichiometric $Au(CN)_x$ surface species or a cluster-type compound of gold is formed.

SAMEVATTING

X-straalfotoëlektronspetrokopie het getoon dat die adsorpsie van goudsianied op koolstof in die aan- of afwesigheid van elektroliete en sure deur dieselfde meganisme geskied. Hoewel die identiteit van die goudsianiedadsorbant onbekend is, het die meganisme blykbaar 'n aanvangsadsorpsiestadium wat die adsorpsie van 'n ionpaar $M^{n+}[Au(CN)_2]_n^-$ behels waar M^{n+} 'n metaalioon (bv. Na^+ , K^+ en Ca^{2+}) met 'n laer oplosbaarheid as die $Au(CN)_2^-$ anioon in die adsorpsiemedium is, gevolg deur 'n trostipe waarin daar 'n oppervlakspezie substoigiometriese $Au(CN)_x$ of 'n trostipe goudverbinding gevorm word.

INTRODUCTION

Activated carbon has already been used successfully in commercial processes¹ that require the removal of small amounts of gold (2 mg.l⁻¹) and silver from cyanide pulps. A number of pilot-plant investigations on the feasibility of using carbon granules in a carbon-in-pulp process² for the recovery and purification of gold and silver from cyanide leach liquors, and in scavenging operations requiring the removal of small amounts of gold (0,2 mg. l⁻¹) from the effluents of gold plants, have proved so encouraging that the large-scale utilization of such processes by the South African gold-mining industry is envisaged. In addition to containing gold and silver anions, typical cyanide leach liquors from gold plants contain relatively large amounts of the cyanide complexes of copper, nickel, cobalt, and iron, which can also be adsorbed on carbon. The best use of carbon in processes for the recovery and purification of gold and silver, not only with respect to the adsorption and elution of these species on carbon, but also in relation to the effective activation and regeneration of the carbon for repeated use, can be achieved only with a sound knowledge of the mechanisms that govern the adsorption of the various metal cyanide species on carbon, and of the factors that influence their adsorption. In spite of the importance of the process, no consensus has been reached regarding the mechanism by which the species are adsorbed on activated carbon.

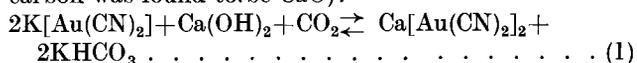
Before the possible adsorption mechanisms are discussed, it is necessary to point out two important facts

that have been confirmed by various workers, including the present authors, regarding the adsorption of gold and silver cyanide on carbon.

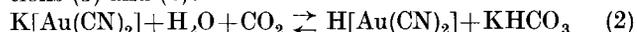
Firstly, the extraction of $Au(CN)_2^-$ and $Ag(CN)_2^-$ is strongly enhanced by the presence of electrolytes such as KCl or $CaCl_2$ in the adsorption medium. Secondly, the adsorption is strongly enhanced by an increase in the acidity of the adsorption medium. Therefore, any acceptable adsorption mechanism has to account for these effects.

Early workers³⁻⁵ postulated a reduction mechanism for the adsorption of aurocyanide on carbon. The reducing agent was usually assumed to be carbon monoxide occluded by the carbon. Feldtmann⁴ proposed the adsorption of an addition compound of the type $AuCN$, CO , $(CN)_2$ on the carbon. However, Allen^{6, 7} subsequently advanced the hypothesis that gold cyanide was adsorbed on carbon without chemical change as $Na[Au(CN)_2]$. This mechanism was generally accepted until Williams⁸ found that the sodium content of a carbon loaded with $Na[Au(CN)_2]$ and then burnt was not sufficient to account for the amount of gold present.

In the 1920s, Gross and Scott⁹ undertook the first detailed investigation of the fundamentals of the adsorption and elution of gold and silver cyanide on carbon. They suggested the following mechanism for the adsorption of gold on activated pinewood carbon, which contains $Ca(OH)_2$ (50 per cent of the ash of this carbon was found to be CaO):



For a sugar carbon that contains no metal ions, they proposed the mechanism given in equation (2). They attributed the improved loading at low pH values to the decomposition of the $Au(CN)_2^-$ and $Ag(CN)_2^-$ complex anions in the presence of acid, according to equations (3) and (4):

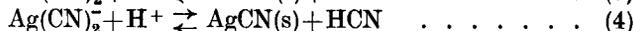
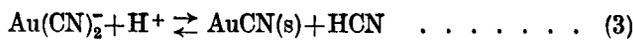


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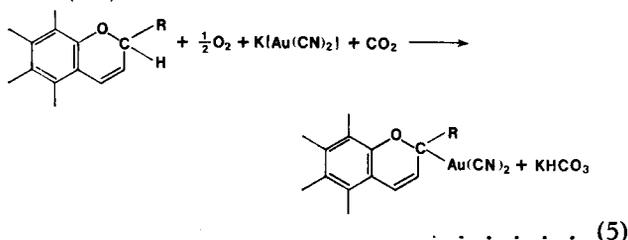
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They therefore thought that highly insoluble AuCN and AgCN were precipitated on the carbon. They attributed the enhanced adsorption in the presence of acid to precipitation, and not to an adsorption mechanism such as that proposed for loading under alkaline conditions.

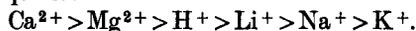
Numerous publications have appeared subsequently in which the mechanisms advanced involve adsorption of the $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ anions on the carbon. Garten and Weiss¹⁰ proposed an alternative mechanism to explain the results of Gross and Scott⁹. They proposed electrostatic attraction of $\text{Au}(\text{CN})_2^-$ anions to positively charged carbonium sites, as in equation (5); as written, this amounts to the rather unlikely oxidation of Au(I) to Au(III):



Kuzminykh and Tjurin¹¹ argued that, since the presence of simple anions in the cyanide solution, even at high concentrations such as 1.5 M, did not affect the capacity of birch and aspen carbons for gold cyanide, the interactions between the $\text{Au}(\text{CN})_2^-$ anion and the carbon were not electrostatic in nature. They proposed that, under acidic conditions, the neutral molecule $\text{HAu}(\text{CN})_2$ is concentrated on the surface of the carbon by a capillary condensation mechanism, whereas, under neutral or alkaline conditions, the $\text{Au}(\text{CN})_2^-$ anion is retained on the carbon together with an equivalent amount of an alkali cation such as K^+ or Na^+ , which is held on the carbon electrostatically. They proposed 'dispersion forces' as being responsible for the retention of the $\text{HAu}(\text{CN})_2$ and $\text{Au}(\text{CN})_2^- - \text{Na}^+$ species on the carbon. Therefore, according to this theory, the nature of the adsorbing form of gold cyanide is different in alkaline and acidic solutions.

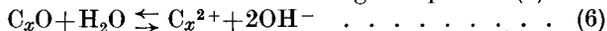
Davidson¹² investigated some of the factors that influence the adsorption of gold on activated coconut-shell carbon under controlled and reproducible experimental conditions. Attempts to reproduce adsorption isotherms under conditions of constant pH value with deionized water failed, and reproducibility could be achieved only in a 0.20M buffer medium of boric acid and 0.20M $\text{KCl} + \text{NaOH}$, at a pH value of 10. He established that the degree of gold adsorption is strongly dependent on the nature and concentration of the 'spectator electrolytes' present in the adsorption medium, and that gold cyanide cannot be adsorbed on carbon in the absence of stabilizing cations such as Na^+ and Ca^{2+} . He advanced a mechanism that involves the adsorption of gold as a metal dicyanoaurate complex: $\text{M}^{n+}[\text{Au}(\text{CN})_2]_n$. In support of this hypothesis, he claimed that, when the cation of the complex M^{n+} is an alkaline earth metal, the complex is bound more firmly to the carbon than when M^{n+} is an alkali metal. He found the strength of adsorption of the $\text{M}^{n+}[\text{Au}(\text{CN})_2]_n$ adsorbate to follow the

sequence



Cho, Dixon, and Pitt¹³⁻¹⁵ investigated the kinetics and thermodynamics of the adsorption of gold and silver cyanide on activated coconut-shell carbon. They found the adsorption rates for both gold and silver cyanide to be controlled by the rate of pore diffusion in the temperature range 25 to 55°C, and the activation energies to be small—8 to 13 $\text{kJ} \cdot \text{mol}^{-1}$. They found that, although the size of the carbon granules affects the initial rate of adsorption, observing faster rates for the smaller size fractions, it has no effect on the equilibrium amount of gold adsorbed. They observed that the equilibrium gold loading, in agreement with the results of other investigators⁹⁻¹², is strongly dependent on the pH value of the adsorption medium, the amount of gold adsorbed in the pH range 4 to 7 being about twice that adsorbed in the pH range 8 to 11.

The mechanism suggested by Cho *et al.* for the adsorption of gold cyanide on carbon involves an electrostatic interaction between $\text{Au}(\text{CN})_2^-$ anions and positively charged sites on the surface of the carbon, as previously suggested by Plaksin¹⁶. They proposed that the positive sites on the carbon are formed in accordance with the theories postulated by Frumkin *et al.*¹⁷⁻¹⁹ to account for the adsorption of acid on carbon. According to these theories, active carbon behaves like an oxygen electrode, and molecular oxygen reacts with the surface of the carbon to form a surface functional group, C_xO or C_xO_2 , which reacts with water according to equation (6):



Cho *et al.* suggested the reaction represented in equation (6) as an explanation for the higher gold capacity observed in acidic solutions, since it would be expected that, at low pH values, the equilibrium would be shifted towards the right, and more positively charged adsorption sites would be produced that would attract an equivalent number of $\text{Au}(\text{CN})_2^-$ anions.

With regard to the adsorption of silver cyanide, they found that, as the loading of silver on the carbon was increased, the zeta potential of the carbon surface became more negative. This led to the postulate that the adsorbate is an anion, $\text{Ag}(\text{CN})_2^-$.

Claus and Weiss²⁰, in studying the adsorption of gold cyanide on various activated carbons, concluded that gold adsorption is not a property of the carbon surface, since certain chemical treatments of the carbon (for example, with a mixture of nitric and hydrochloric acids at 80°C) prevent gold adsorption. Although it is believed that gold adsorption is related to specific functional groups or 'points of attachment' on the carbon, they excluded the involvement of basal planes, carboxylic acid groups, and basic oxides. However, they pointed out that a special type of micropore might be involved.

Recently, Cho and Pitt^{21, 22} made a detailed investigation of the factors that influence the adsorption of silver cyanide on activated coconut-shell carbon. Although they concluded that the $\text{Ag}(\text{CN})_2^-$ anion is adsorbed, they excluded an electrostatic interaction between the $\text{Ag}(\text{CN})_2^-$ anions and positive sites on the carbon surface, at least for adsorption from alkaline

solutions. Instead, they advanced an adsorption mechanism that is in accordance with the ionic solvation-energy theory developed by Andersen and Bockris²³ to account for the specific adsorption of anions on metal electrodes. According to this model, the degree and type of ionic hydration are the principal factors that determine specific adsorption. Applied to carbon, the theory predicts that a large, weakly hydrated anion such as $\text{Ag}(\text{CN})_2^-$ will be specifically adsorbed on the carbon surface after losing some of its primary-hydration water molecules, whereas small anions with a large number of strongly bound water molecules in their primary hydration shells, for example CN^- , will not be specifically adsorbed and will therefore remain in the outer part of the electrical double layer.

The capacity of carbon for the $\text{Ag}(\text{CN})_2^-$ anion is considerably higher than for the CN^- anion, and Cho and Pitt regarded this as proof of the applicability of the Andersen and Bockris model to the adsorption of anions on carbon. They also found that the small, highly hydrated Na^+ cation is adsorbed on carbon only if it is present in solution with $\text{Ag}(\text{CN})_2^-$ anions, and not if it is present alone with small, highly hydrated anions such as CN^- . They obtained similar results for the Ca^{2+} cations.

Confirming the results of other researchers¹² on the adsorption of gold cyanide, Cho and Pitt^{21, 22} found that an increase in the concentration of K^+ , Na^+ , and Ca^{2+} ions in solution enhances the adsorption of silver cyanide on carbon. To account for these 'ionic-strength' effects, they proposed that the Na^+ , K^+ , and Ca^{2+} ions are non-specifically adsorbed on the silver cyanide complex, which in turn is specifically adsorbed on the carbon surface, and that these ions provide additional sites for the adsorption of anions such as $\text{Ag}(\text{CN})_2^-$ and CN^- . Therefore, the picture that emerges is of a multilayer adsorption (supposedly consistent with the modern view of the electrical double layer) as depicted in Fig. 1.

The deleterious effect of the free CN^- anion on the adsorption of the $\text{Ag}(\text{CN})_2^-$ anion (although CN^- is not specifically adsorbed on the carbon) is believed to be related to competitive non-specific adsorption on the cation sites between the $\text{Ag}(\text{CN})_2^-$ and CN^- anions.

The capacity of carbon for gold cyanide is about three times higher than for silver cyanide. Cho and Pitt attributed this to the larger ionic radius of gold (13,7 nm) compared with that of silver (12,6 nm), consistent with the solvation-energy theory.

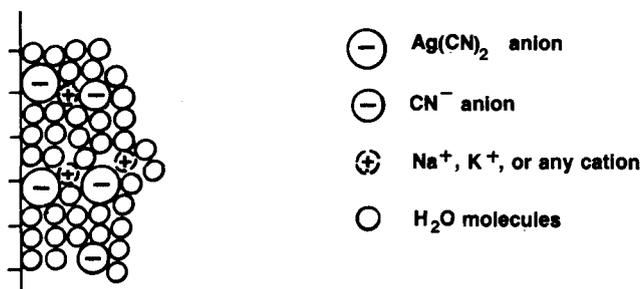
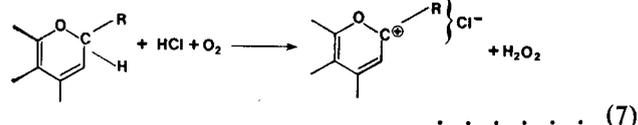


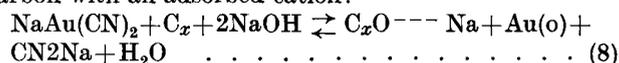
Fig. 1—Schematic representation of the Cho model for the mechanism of adsorption of $\text{Ag}(\text{CN})_2^-$ on carbon

The enhanced adsorption of silver cyanide in the presence of an acid was attributed to a different mechanism, consistent with the model postulated by Garten and Weiss¹⁰ to account for the adsorption of hydrochloric acid on carbon in the presence of molecular oxygen, as represented in equation (7):



This mechanism assumes the presence on the carbon of chromene functional groups that are readily oxidized in the presence of acid to carbonium ions, and Cho²¹ postulated that the $\text{Ag}(\text{CN})_2^-$ anion is adsorbed on these positive sites by an electrostatic interaction. However, he pointed out that such positive sites can also be formed in accordance with the theories of Frumkin *et al.*¹⁷⁻¹⁹. Therefore, he assumed the adsorption of $\text{Ag}(\text{CN})_2^-$ on carbon from acidic medium to be dependent on the surface charge of the carbon.

On the other hand, Grobovskii and his co-workers²⁴, after investigating the adsorption of gold on carbon manufactured from phenol-formaldehyde resin, concluded that the adsorption of gold is accompanied by reduction of the $\text{Au}(\text{CN})_2^-$ complex to metallic gold. Their investigation²⁵ into the elution of gold adsorbed on coal carbon from cyanide solution showed that complete elution of the gold can be achieved only if a gold-complexing agent such as CN^- or CNS^- is present in the eluant. This gives credence to the hypothesis of a reduction mechanism as the responsible reactions. They consider¹ that the role of carbon as the reducing agent is in accordance with the reaction shown in equation (8), where $\text{C}_x\text{O}^{---}\text{Na}$ represents the oxidized surface of the carbon with an adsorbed cation:



The present state of thinking on the mechanism of the adsorption of aurocyanide on activated carbon can be summarized as follows. The theories fall into three categories:

- (1) those proposing that the gold is present as an aurocyanide ion^{6, 7-10, 12, 13},
- (2) those suggesting that gold is present as a compound other than the aurocyanide ion (e.g., precipitated AuCN^4 ,^{9, 11}, and
- (3) those proposing that the aurocyanide is reduced to metallic gold²⁴.

Much of the controversy surrounding the adsorption mechanism undoubtedly relates to the fact that the carbon is not readily amenable to physical investigation by techniques such as infrared spectroscopy. Therefore, very little information is available about the surface functional groups present on the carbon^{10, 26, 27}, and about the nature of the adsorbed gold and silver cyanide species.

The technique of X-ray photoelectron spectroscopy (XPS) enables one to decide on the oxidation state of an element. Therefore, this technique was used at the National Institute for Metallurgy to distinguish between possibilities (1) and (2) above on the one hand, and possibility (3) on the other, since the first two possibilities

require the gold to have an oxidation state of 1, and the third requires an oxidation state of 0. Also thought to be worth while was re-investigation of the effect of factors such as pH and ionic medium on the loading, not only of gold cyanide, but also of other metal ions and their complexes, because the behaviour of the latter might shed some light on the mechanism of adsorption. For example, mercury (II) forms the cyanide complex $[\text{Hg}(\text{CN})_2]$, which resembles $[\text{Au}(\text{CN})_2]^-$ in all respects except that it is not an anion, and its loading behaviour should indicate whether ionicity is at all important in the adsorption by activated carbon. Another simple approach to the problem of whether the gold is present as $[\text{Au}(\text{CN})_2]^-$ involves the analysis of loaded carbons for their gold and nitrogen contents, which would indicate how many cyanide ions are associated with the gold on the carbon.

EXPERIMENTAL METHOD

Origin and Pretreatment of Carbon

Unless otherwise stated, the product used throughout this investigation was granular (0,5 to 2 mm), high-temperature, steam-activated carbon, type G210, supplied by Le Carbone SA (Pty) Ltd. Prior to its use, the carbon was washed thoroughly with hot deionized water by successive soaking and decantation, and was then allowed to dry in air. The surface area of the carbon, measured by the nitrogen BET method, was found to be about $1\ 000\ \text{m}^2\cdot\text{g}^{-1}$.

Chemicals

The potassium dicyanoaurate used in this investigation was supplied by Johnson Matthey, and all the other chemicals used were of A.R. grade.

Loading Kinetics

Data on the rate of adsorption of gold cyanide were obtained by contacting a known mass of carbon (either

0,25 g or 0,50 g) with 300 ml of solution containing a known amount of $\text{KAu}(\text{CN})_2$ (usually 200 mg of gold per litre) in the apparatus^{13, 21} shown in Fig. 2. Basically, the apparatus consists of a sealed glass reactor of 500 ml capacity, in which the gold-containing solution is pumped through a bed of carbon that is supported on a sintered-glass plug immersed in the solution. The tests were conducted under an atmosphere of nitrogen (unless otherwise stated) in the presence or absence of electrolytes and acids. The reactor was jacketed so that tests could be conducted at different temperatures.

The pH value of the adsorption medium was monitored continuously with a glass electrode and maintained at the desired value by the addition of either potassium hydroxide or hydrochloric acid. The solution was agitated with a magnetic stirring bar, and solution samples, usually of 3 ml, were taken at regular intervals and analysed for their metal-ion content by atomic-absorption spectrophotometry (AAS), so that the reaction kinetics could be determined.

Initial tests indicated that a solution flow-rate of 10 to $70\ \text{ml}\cdot\text{min}^{-1}$ through the carbon bed had only a small effect on the rate of adsorption of gold cyanide on carbon, and all the subsequent experiments were conducted at a flow-rate of about $50\ \text{ml}\cdot\text{min}^{-1}$.

Equilibrium Adsorption Tests

A batch technique was used in these tests. A known mass of carbon (usually 0,25 g) was agitated for 24 hours with 50 ml of a solution containing a known amount of dissolved gold complex, which varied from 10 to 800 mg/l, in the presence or absence of electrolytes and acids. For practical reasons, this agitation time was regarded as resulting in an effective equilibrium. (This aspect is dealt with in greater detail later.) The solutions were contained in plastic bottles, and were mixed by a mechanical roller, which rolled the bottles. The metal

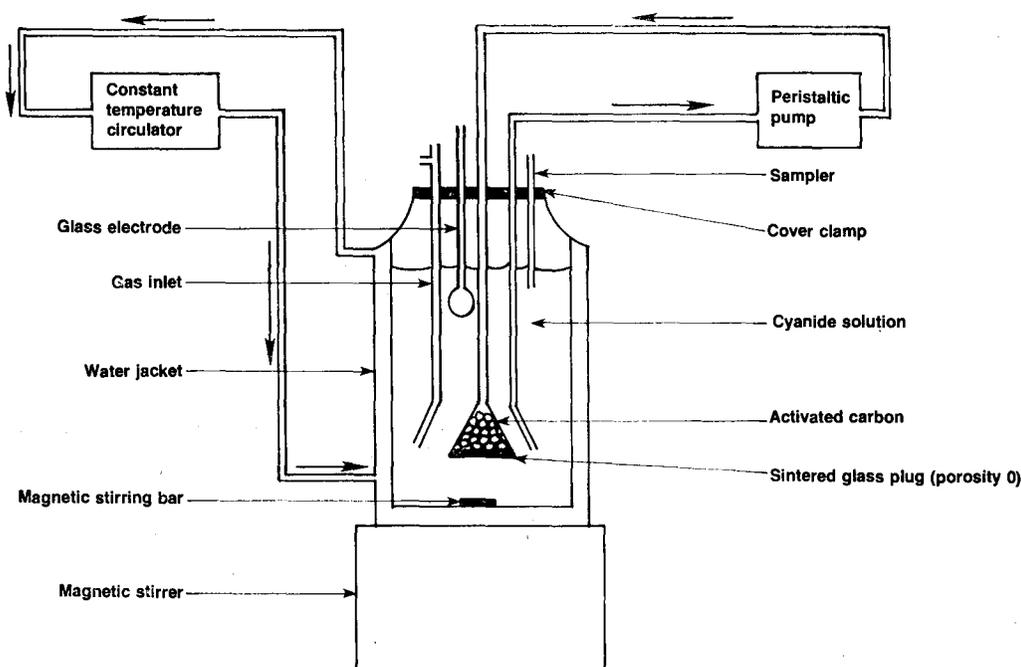


Fig. 2—Flow system for the contacting of carbon with gold cyanide solution

loading on the carbon was calculated from the difference between the metal contents of the initial and final solutions as determined by AAS.

Measurement of the Reduction Potential of Carbons

The reduction potential of at least 20 granules of carbon having approximately the same size and shape was measured for each type of carbon.

The reduction potentials were then measured against a calomel electrode, the carbon granules being contacted with a graphite-rod electrode, which was covered with heat-shrinkable tubing that exposed only the end face to the solution. The measurements were done in 0,01 M NaCl solution at a pH value of 5,0 after the granules had been allowed to soak in this solution for 15 minutes.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a relatively new experimental technique in the determination of the binding energy of electrons in atoms or molecules. Since the technique has shown that the binding energies of core electrons in an atom or ion depend on the distribution of the valence charge and thus gives information about the oxidation state of the atom or ion²⁸, this technique was used in the study of gold-loaded carbons.

For gold, the ejection of an electron from the filled 4f shell gives a spectrum in which the photoemission valence band is split because of spin-orbit coupling effects. The two bands correspond to the $4f(\frac{5}{2})$ and $4f(\frac{7}{2})$ components. Since a core electron belonging to an ion, for example Au(III), is bound more strongly by the nucleus than a

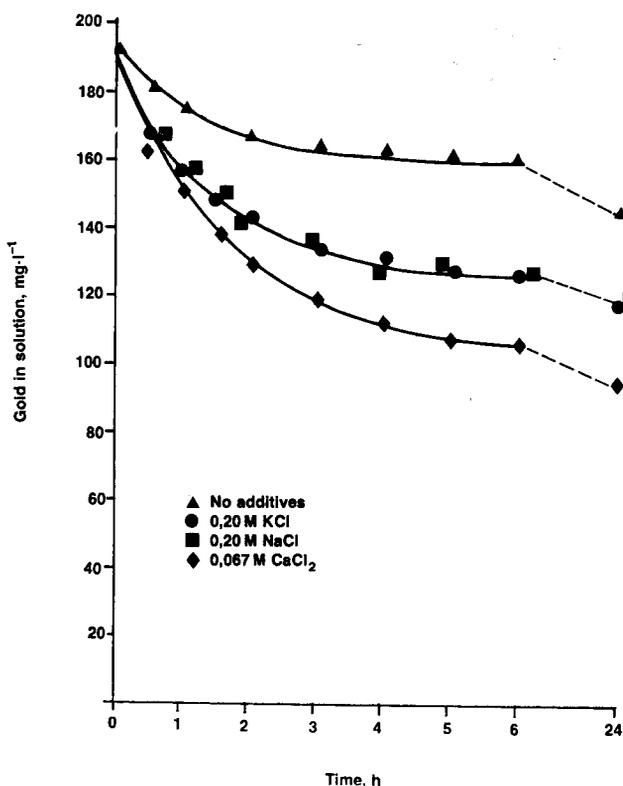


Fig. 3—Rate curves for the adsorption of aurocyanide on carbon in the absence or presence of electrolytes at the same ionic strength (experimental conditions: volume of solution 300 ml, mass of carbon 0,25 g, pH 10,0, nitrogen atmosphere, ionic strength 0,20 M, initial concentration of gold 192 mg.l⁻¹)

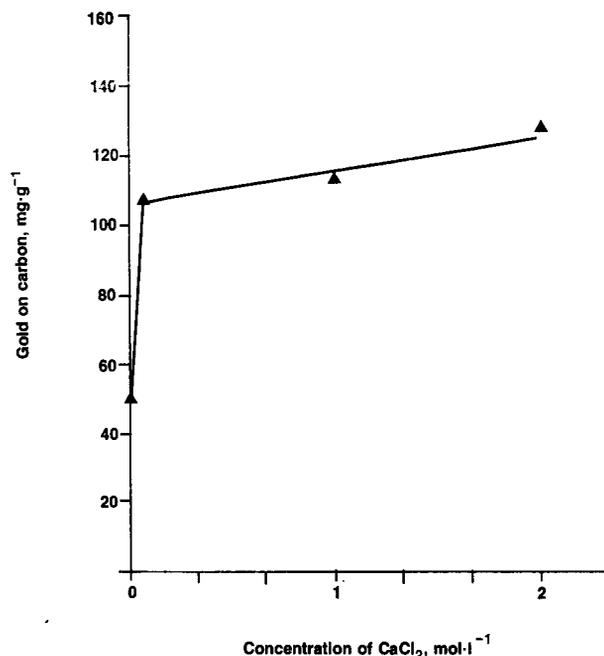


Fig. 4—Effect of the ionic strength of the adsorption medium on the gold capacity of carbon (experimental conditions: volume of solution 300 ml, mass of carbon 0,25 g, pH 10,0, nitrogen atmosphere, initial concentration of gold 192 mg.l⁻¹)

TABLE I

EFFECT OF TIME ON THE AMOUNT OF GOLD ADSORBED ON CARBON*

Time	Gold in solution mg.l ⁻¹
0	596
24 hours	350
1 week	340
2 weeks	325
3 weeks	305
12 weeks	275

* These tests were conducted by the batch technique with 50 ml of solution containing only KAu(CN)₂ and 0,25 g of carbon.

similar electron in an uncharged atom, for example Au(0), the binding energy of the core electrons in the former instance will be greater than that of metallic gold. This technique was therefore used in the determination of the oxidation number of gold in gold cyanide species that have been adsorbed on carbon in the presence or absence of electrolytes, and under acidic or alkaline conditions. For comparison, the XPS spectra of Au(0) and Au(I) in KAu(CN)₂ were also recorded.

The XPS spectra were recorded with an AEI-KRATOS ES 200 B spectrometer, and a magnesium X-ray source was used. The pressure in the analyser chamber was between 10⁻⁹ and 10⁻¹⁰ kP. The binding energy of the core electrons was calculated only for the $4f(\frac{7}{2})$ component of the doublet, and the C 1S photoemission valence band of the carbon in coconut-shell carbon was used as the internal reference (relative to C 1S at 285 eV).

RESULTS AND DISCUSSION

Factors Influencing the Adsorption of Aurocyanide on Carbon

Ionic Medium

Fig. 3 shows the effect of various ionic media on the

adsorption of aurocyanide on activated carbon from a solution containing initially 192 mg of dissolved gold per litre. It is apparent that, in all cases, the rate at which the gold is taken up slowed down considerably after 6 hours. Even after 3 months, true equilibrium was not obtained (see Table I), but the rate of loading after 24 hours was extremely slow, and this was therefore taken for practical reasons as the effective equilibrium loading. Fig. 3 shows that, as found by previous workers, added sodium or potassium ions enhance loading¹², and the same concentration of calcium in turn increases the loading still further. It might be considered that the results in Fig. 3 are due to an ionic-strength effect, since a divalent ion will produce an ionic strength (μ) greater than an equivalent concentration of univalent ions; μ is given by $\frac{1}{2} \sum C_i Z_i^2$, where C_i is the concentration in moles per litre of species i , and Z_i is the charge on i . For CaCl_2 , $\mu = 3C$, whereas, for KCl , $\mu = C$. However, concentrations of KCl three times as high as CaCl_2 do not produce a loading enhancement of anything like as much. As seen in Fig. 4, the enhancement of loading has a dramatic effect with only a very small quantity of added electrolyte, and thereafter increases only slightly. This is not in keeping with a simple ionic-strength effect. One is forced to conclude from Fig. 4 that a cation such as calcium is specifically involved in the adsorption of the aurocyanide ion.

An important factor to be considered in relation to the adsorption of $\text{Au}(\text{CN})_2^-$ as a simple anion on the carbon is the effect on its adsorption of other simple anions that might be expected to compete directly with it for adsorption sites. Fig. 5 shows the equilibrium adsorption isotherms, plotted as milligrams of gold adsorbed per gram of carbon, versus the equilibrium gold concentration in milligrams per litre obtained at an ionic strength, μ , of 8×10^{-2} M in KCN , KCl , CaCl_2 , and NaClO_4 , and in HNO_3 with $\mu = 10^{-2}$ M. Each point on the isotherm represents a different initial concentration of gold. The

concentration was varied between 10 and 1 000 mg of gold per litre. These isotherms show that the highest loading occurs in acid solutions, whereas the lowest loading is found in the absence of added electrolytes. With Cl^- as the common anion, Ca^{2+} at the same ionic strength produces a higher gold capacity than K^+ . In the presence of a common cation K^+ (or Na^+ since the rate curves in Fig. 3 indicate that Na^+ and K^+ have a very similar effect on the gold adsorption), the loading is slightly higher if the anion is Cl^- rather than CN^- or ClO_4^- . The results in Fig. 4 show that the maximum capacity of carbon for the adsorption of gold from solutions that contain high concentrations of CaCl_2 , viz 2 M, is about 120 mg of gold per gram of carbon, whereas, under the same experimental conditions, the maximum capacity of carbon for the adsorption of gold from a solution containing only 0.1 M hydrochloric acid (see Fig. 5), is about 180 mg of gold per gram of carbon. Therefore, the additional gold adsorption that occurs under acidic conditions cannot be accounted for simply in terms of an ionic-strength effect, and must be inherently associated with pH. It can also be inferred from these results that ionic-strength and acidic effects are due to thermodynamic, and not kinetic, considerations.

It is normally found that a weakly hydrated anion such as ClO_4^- will load as well as $\text{Au}(\text{CN})_2^-$ onto simple anion-exchange resins. Therefore, it would be expected that the presence of ClO_4^- anions together with $\text{Au}(\text{CN})_2^-$ anions would have a marked influence on the gold capacity of the resin, and that the amount of gold loaded would decrease as the concentration of ClO_4^- anions in the adsorption medium increased. On the other hand, small, highly hydrated anions such as Cl^- would not be expected to influence the loading of $\text{Au}(\text{CN})_2^-$ onto an anion-exchange resin. This is confirmed by the results in Table II, which compares the effect of 8×10^{-2} M Cl^- anions and 8×10^{-2} M to 2.4×10^{-1} M ClO_4^- anions in

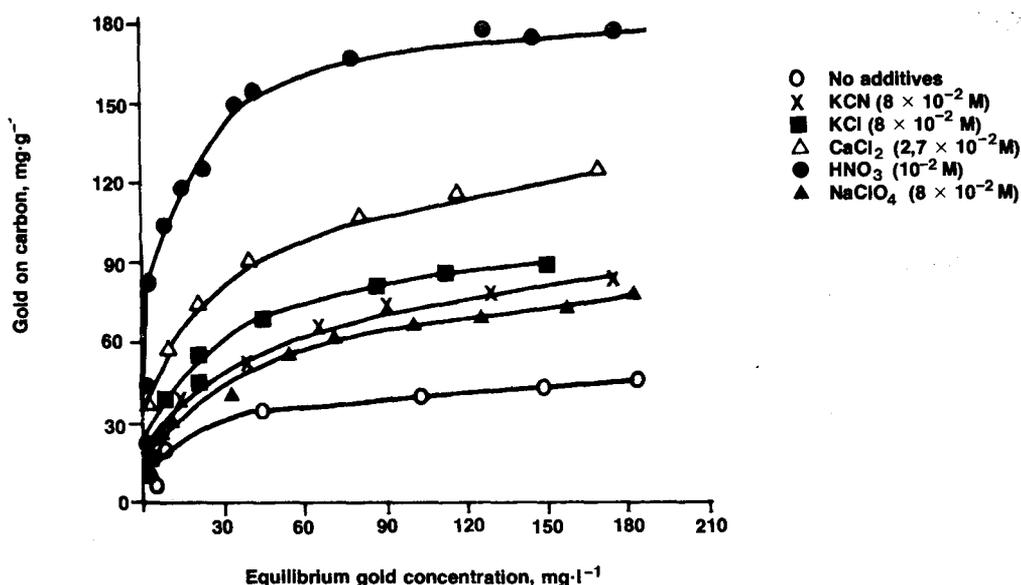


Fig. 5—Equilibrium adsorption isotherms for gold cyanide on carbon in the presence of various electrolytes at the same ionic strength (experimental conditions: volume of solution 50 ml, mass of carbon 0.25 g)

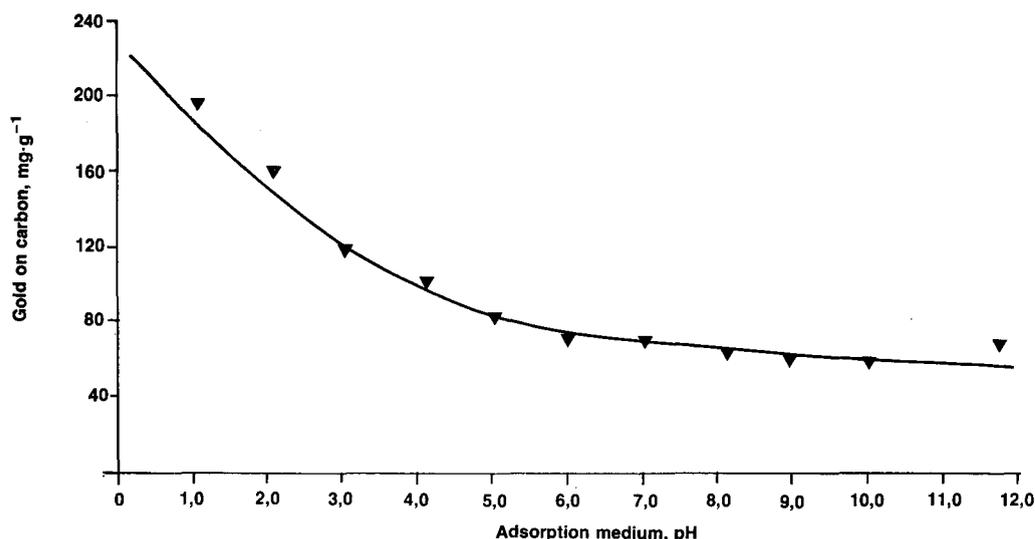


Fig. 6—Effect of the pH value of the adsorption medium on the gold capacity of the carbon (experimental conditions: volume of solution 300 ml, mass of carbon 0,25 g, nitrogen atmosphere, initial concentration of gold 190 mg.l⁻¹)

TABLE II
EFFECT OF ClO₄⁻ AND Cl⁻ IONS ON THE ADSORPTION OF Au(CN)₂⁻ ON CARBON AND ON IRA 400*

Composition of solution	Gold adsorbed, mg.g ⁻¹	
	Carbon	IRA 400
500 mg.l ⁻¹ Au + 8 × 10 ⁻² M NaCl	74,6	95,6
500 mg.l ⁻¹ Au + 8 × 10 ⁻² M NaClO ₄	69,0	45,6
500 mg.l ⁻¹ Au + 1,6 × 10 ⁻¹ M NaClO ₄	70,6	32,2
500 mg.l ⁻¹ Au + 2,4 × 10 ⁻¹ M NaClO ₄	68,6	21,6

* Experimental conditions:

- (1) Volume of solution 50 ml
- (2) Mass of carbon or resin 0,25 g
- (3) Equilibrium time 24 h

the adsorption medium on the amount of gold loaded onto IRA 400 (in the Cl⁻ form) and carbon. The results in Table II indicate that carbon behaves quite differently from an anion-exchange resin with respect to the adsorption of gold cyanide, in that an increase in the amount of ClO₄⁻ in solution by a factor of 3 does not influence the gold capacity, and that, at an ionic strength of 8 × 10⁻² M, the gold capacity is marginally less if the competing anion is ClO₄⁻ rather than Cl⁻.

Therefore, the observation that the presence of an excess of ClO₄⁻ anions at a ClO₄⁻ to Au(CN)₂⁻ ratio of between 26 : 1 and 315 : 1 (see Fig. 5) does not greatly depress the gold loading on carbon militates against the adsorption of Au(CN)₂⁻ anions on carbon by simple electrostatic interactions in the electrical double layer, or with positively charged sites on the carbon surface.

Acidity of the Adsorption Medium

The variation in the amount of gold adsorbed at equilibrium from a solution initially containing 190 mg of gold per litre as a function of the pH value of the adsorption medium is shown in Fig. 6. The pH value of the adsorption medium was adjusted by the addition of hydrochloric acid to the solution, no other additives being present. The results indicate that the equilibrium gold

adsorption is virtually independent of the pH value in the range 12 to 6, whereas the gold capacity increases strongly with pH values in the range 5 to 1. Under these experimental conditions, the maximum adsorption is 60 mg of gold per gram of carbon at pH 12, compared with 200 mg of gold per gram of carbon at pH 1,0. One finds that, parallel with the invariance of the loading above a pH value of 6,0, the rate of loading is constant at pH 6,0, but below that value it increases with decreasing pH.

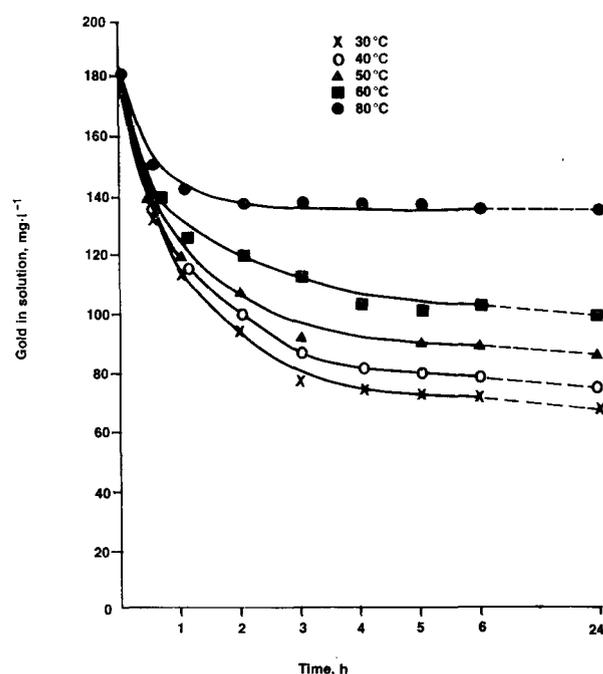


Fig. 7—Rate curves for the adsorption of aurocyanide on carbon at temperatures in the range 30 to 80°C (experimental conditions: volume of solution 300 ml, mass of carbon 0,25 g, nitrogen atmosphere, initial concentration of gold 180 mg.l⁻¹, adsorption medium contained 2,8 g of CaCl₂ and 0,5 g of KCN per litre)

Temperature

The effect of temperature in the range 30 to 80°C on the rate of adsorption of gold onto activated carbon from a solution containing initially 180 mg of gold, 2,8 g of CaCl₂, and 0,5 g of KCN per litre is shown in Fig. 7. Fig. 8 shows the equilibrium amount of gold adsorbed on the carbon (in micromoles of gold per gram of carbon) as a function of the equilibrium gold concentration (in millimoles per litre of solution) at various temperatures in the range 22 to 79°C. The initial amount of gold in solution was varied in the range 10 to 600 mg/l. The isotherms show that the equilibrium gold loading decreases markedly as the temperature of the adsorption medium is increased. From these isotherms it is readily apparent why good elution can be achieved²⁹⁻³¹ only at high temperatures. The reason for this behaviour is possibly related to solubility considerations. For example, the solubility of KAu(CN)₂ in hot water is about fourteen times greater than in cold water.

The equilibrium loading as a function of temperature can be used to give an estimate of the isosteric heat of adsorption^{15, 21}, which is defined as the enthalpy change accompanying the adsorption of one mole of adsorbate at constant surface coverage. The mathematical form of the isosteric heat equation is

$$\ln C = -\frac{q}{R} (1/T) + \text{constant},$$

where C is the equilibrium concentration of gold in solution at constant gold loading for a particular temperature, q is the isosteric heat, T is the absolute temperature, and R is the gas constant. Plots of $\ln C$ versus $1/T$ gave a set of linear relations, the slopes of which were used in the calculation of the isosteric heat of adsorption for gold loadings in the range 25 to 300 μmol of gold per

gram of carbon. An average value of 42 kJ.mol⁻¹ was found. However, there were insufficient data at low surface coverages for a check to be made of whether the adsorption of gold cyanide is also characterized by a more exothermic reaction at low surface coverages, as was claimed for the adsorption of Ag(CN)₂⁻ on carbon^{15, 21}.

Also, the fact that the adsorption of aurocyanide on carbon is a considerably exothermic process does not accord well with the idea that a simple ion-exchange process is involved. Thus, it is normally found that the effect of temperature on ion-exchange equilibria is very small³², whereas it is sufficiently large here to be a vital component in rendering the carbon strippable.

XPS Investigation

The 4f($\frac{7}{2}$) binding energies of gold metal and KAu(CN)₂, together with the binding energies for the carbons that were loaded with gold under specified conditions, are shown in Table III. From the values of the binding energies of gold in the various gold-loaded carbons, which are the same within the limits of experimental error (91,6 eV), it can be concluded that the gold cyanide compound adsorbed on the carbon is always the same, and is therefore independent of the composition of the adsorption medium.

The values given in the literature for the relative shift in the binding energies of Au(I) in a variety of mono-nuclear compounds relative to metallic gold (i.e., with Au(0) vary³³ between 1,5 and 2,3 eV. Since the binding energy of the gold cyanide species that is adsorbed on the carbon is only 0,7 to 0,8 eV above that observed for Au(0) (viz, 90,8 eV), these results suggest that Au(CN)₂⁻ is adsorbed on carbon by a reduction

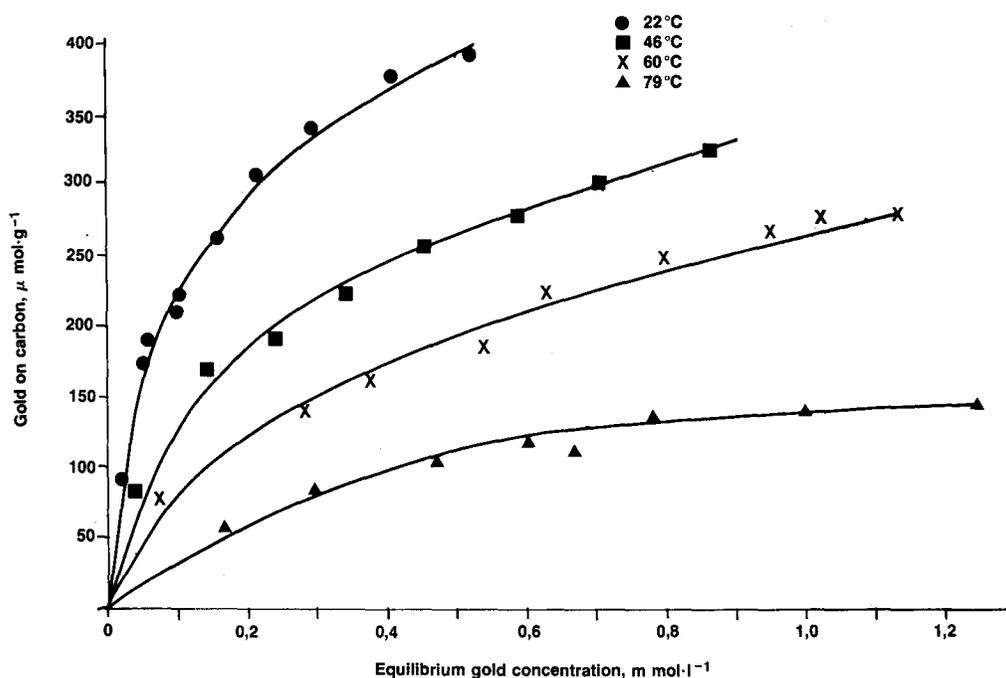


Fig. 8—Equilibrium adsorption isotherms for gold cyanide on carbon at different temperatures (experimental conditions: volume of solution 50 ml, mass of carbon 0,25 g, adsorption medium contained 2,8 g of CaCl₂ and 0,5 g of KCN per litre)

mechanism. The XPS spectra of Au(I) in $\text{KAu}(\text{CN})_2$, of gold metal adsorbed on carbon from a solution of AuCl_4^- , and of gold adsorbed on carbon from a solution containing $\text{Au}(\text{CN})_2^-$ anions are shown in Fig. 9. The small shift between the $4f(7/2)$ levels of Au(0) and gold adsorbed on carbon from cyanide medium is apparent. It has been proposed⁹ that $\text{Au}(\text{CN})_2^-$ is adsorbed on carbon by precipitation of insoluble AuCN in the pores of the carbon. As a definite value for the binding energy of the Au(I) in the AuCN polymer was not ascertained owing to a reference problem in the XPS investigation, the adsorption of AuCN on carbon from a solution containing $\text{Au}(\text{CN})_2^-$ anions cannot be excluded.

Nevertheless, if it is assumed that the operative reduction mechanism is one in which a unique gold cyanide species is formed and adsorbed on the carbon, and also that a linear relationship exists between the binding energies of the $4f(7/2)$ level and the oxidation state of the gold in the gold compound, as suggested by the work of Knecht *et al.*³⁴, then a binding energy of 91,6 eV would correspond to the presence on the carbon of a gold compound in which the gold atoms have an oxidation number of 0,3.

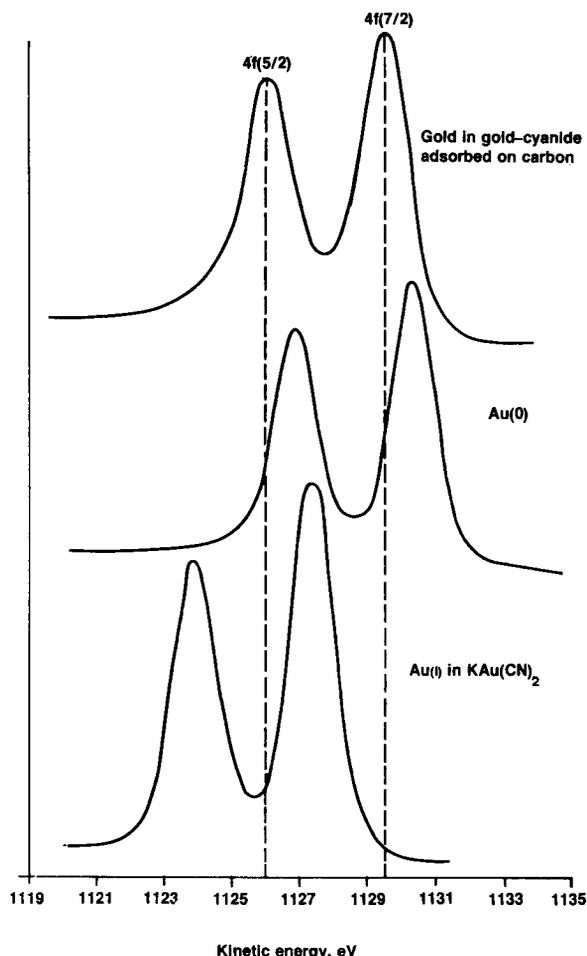


Fig. 9—X-ray photoelectron spectra (Au 4f doublet) for gold metal, for gold(I) in $\text{KAu}(\text{CN})_2$, and for gold adsorbed on carbon

TABLE III

CORE LEVEL $4f(7/2)$ BINDING ENERGIES FOR SOME GOLD COMPOUNDS AND CARBONS[†] CONTAINING ADSORBED GOLD, RELATIVE TO CARBON IS AT 285 eV*

Material	Binding energy [†] eV
<i>Gold compounds</i>	
Au metal	90,8
Au(I) in $\text{KAu}(\text{CN})_2$	93,6
<i>Gold-loaded carbons</i>	
Only $\text{KAu}(\text{CN})_2$	91,5
$\text{KAu}(\text{CN})_2 + 0,1 \text{ M HNO}_3$	91,5
$\text{KAu}(\text{CN})_2 + 0,1 \text{ M CaCl}_2$	91,6
$\text{KAu}(\text{CN})_2 + 0,1 \text{ M KCl}$	91,5
$\text{KAu}(\text{CN})_2 + 0,1 \text{ M KCN}$	91,6
Carbon from Fairview Mine, Barberton	91,6

* The gold loading on the carbons varied from 1 to 15 per cent.
[†] The standard deviation on all these values is 0,3 eV.

TABLE IV

NITROGEN CONTENT OF GOLD-LOADED CARBONS*

Gold on carbon	Composition of adsorption medium	Nitrogen content of carbon if $\text{Au}(\text{CN})_2^-$ adsorbed	Nitrogen content from micro-analysis [†]
%		%	%
3,4	} $\text{KAu}(\text{CN})_2 + 10^{-2} \text{ M HNO}_3$	0,48	0,40
5,8		0,82	0,43
7,3		1,04	0,80
14,1		2,00	1,11

* The results reported here are the average values obtained from at least three determinations.
[†] The nitrogen content of virgin carbon is 0,1 per cent, and this has been subtracted from these values.

Nitrogen Content of Gold-loaded Carbons

The nitrogen contents of various carbons containing a known amount of gold that was adsorbed on the carbon under alkaline or acidic conditions, together with the amount of nitrogen that would be predicted on the assumption that the adsorbate is the $\text{Au}(\text{CN})_2^-$ anion, are shown in Table IV. The nitrogen contents were determined by elemental micro-analysis, and the results indicate that the amount of nitrogen found on the carbon is always less than that required for the adsorption of $\text{Au}(\text{CN})_2^-$ anions, and that the ratio of gold to nitrogen approaches 1 : 1 at high loadings from either alkaline or acidic solutions.

Before the carbons were analysed for their nitrogen content, they were washed with water and allowed to dry in air for 2 days. Carbon is a well-known catalyst for the oxidation of CN^- to NH_3 , and it is therefore possible that the low nitrogen content of the gold-loaded carbons can be explained as being due to a loss of NH_3 . Measurements of the free cyanide in solution by an electrochemical technique showed that no detectable amounts of cyanide are liberated into solution during the adsorption of $\text{Au}(\text{CN})_2^-$ on activated carbon from a solution initially containing 330 mg of gold per litre. Thus, if cyanide is lost from $\text{Au}(\text{CN})_2^-$ on adsorption, it is not released into solution and the above results must be treated with caution.

Adsorption of Aurocyanide on Carbon

Various workers have used the Freundlich^{11, 12,}

Langmuir^{13, 15, 21}, and Temkin¹¹ models to analyse their adsorption data, and have drawn conclusions as to the nature of the adsorption process according to which of these models best fitted the data. A serious criticism that must be levelled at these approaches is that all these models were derived on the assumption that the adsorption process is reversible (i.e., that there is a reasonably rapid exchange between adsorbed $\text{Au}(\text{CN})_2^-$ ions and those in the bulk solution). This would be evidenced by a re-adjustment of the equilibrium after it had been disturbed. For example, when the bulk solution is removed and replaced with water, gold should desorb from the carbon to re-establish a new equilibrium, and this, as shown by the present work, does not occur.

A further criticism is that Cho *et al.*¹⁴, for example, allowed only 4 hours for equilibrium, whereas the present investigation showed that true equilibrium had not been achieved even after 3 months. This means that the fitting of various models to the isotherms so obtained has only empirical validity.

The results of the present XPS investigation indicate that the adsorption of aurocyanide on carbon from acidic or alkaline solutions, in the presence or absence of electrolytes, may proceed by a reduction mechanism. The following also support a reduction mechanism, or militate against the idea that $\text{Au}(\text{CN})_2^-$ anions are adsorbed on carbon by simple electrostatic interactions in the electrical double layer or with positively charged sites on the surface of the carbon.

- (1) If the solvation-energy theory proposed by Cho and Pitt^{21, 22} fully explained the adsorption of $\text{Au}(\text{CN})_2^-$ anions on carbon, it would be expected that the presence of excess ClO_4^- anions in the adsorption medium, which like the $\text{Au}(\text{CN})_2^-$ are large and weakly hydrated and therefore strongly extracted by anion exchangers, would markedly depress the adsorption of $\text{Au}(\text{CN})_2^-$ on carbon by competition for adsorption sites. However, although a comparison of the adsorption isotherms obtained in the presence of Cl^- and ClO_4^- (see Fig. 5) indicates a slightly lower gold capacity with ClO_4^- , the depression is not nearly as marked as that observed with IRA 400 (Table II).
- (2) Elution tests on gold-loaded carbons have indicated that the adsorbed gold can be effectively eluted only if an anion that is able to form strong complexes with gold (e.g., CN^- or SCN^-) is present in the eluant, or if the carbon is pretreated with CN^- prior to its elution with hot water. This is demonstrated in Fig. 10, which shows the elution of gold with hot water (90°C) from a gold-loaded carbon after the carbon had been pretreated with 1 bed volume of each of the following: 5 per cent NaOH, a mixture of 2 per cent NaCN and 2 per cent NaOH, and 5 per cent NaCN. These results are in agreement with those obtained by Grabovskii *et al.*²⁵.
- (3) Fig. 11 shows how the reduction potential of various carbons manufactured from coconut shells and bituminous coal affects the amount of gold adsorbed from a solution containing initially 250 mg of gold per litre. The results indicate that, the higher the

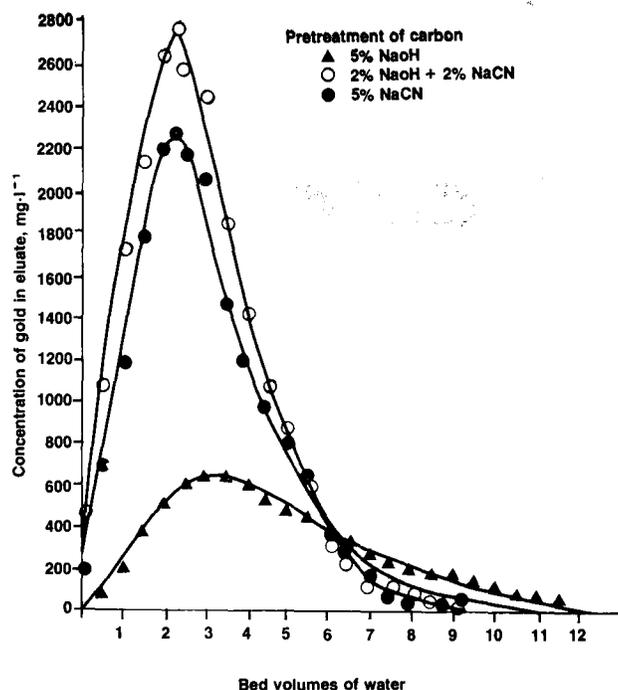


Fig. 10—Elution profiles for the desorption of gold from carbon with hot water (90°C) as the eluant after pretreatment of the carbon with 5 per cent NaOH, 2 per cent NaOH and 2 per cent NaCN, and 5 per cent NaCN (experimental conditions: volume of carbon 120 ml, loading on carbon 18 300 mg of gold per kilogram of carbon, temperature 90°C)

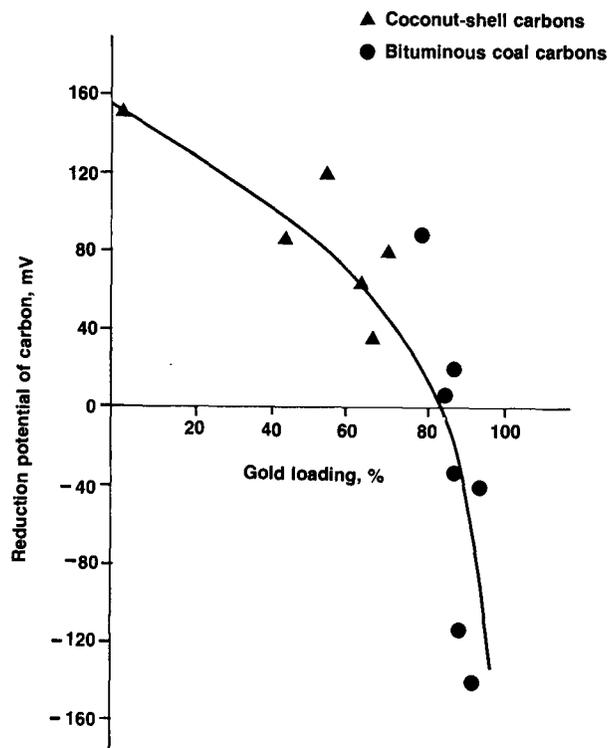


Fig. 11—Effect of the reduction potential of various carbons manufactured from coconut shells and bituminous coal on the amount of gold adsorbed on the carbons from a solution containing 250 mg of gold as $\text{KAu}(\text{CN})_2$ per litre

reducing power of the carbon, the higher its capacity for gold.

- (4) It is well known that gold is adsorbed on carbon from a solution containing $\text{Au}(\text{Cl})_4^-$ anions by reduction of the complex to metallic gold, which can be detected visually on the external surface of the carbon particles. For a series of carbons that vary in their reducing power, a linear correlation was found between the amount of gold cyanide adsorbed on the carbon and the amount of metallic gold precipitated on the same carbon for adsorption from a solution containing $\text{Au}(\text{Cl})_4^-$ anions (see Fig. 12).
- (5) Oxidation of the surface functional groups of an active carbon with, for example chlorine, results in a marked decrease in the ability of the carbon to adsorb gold cyanide or metallic gold from a solution of $\text{Au}(\text{Cl})_4^-$ anions (see Table V). Oxidation of surface functional groups also explains the observation by Claus and Weiss²⁰ that treatment of an active carbon with a mixture of HNO_3 and H_2SO_4 at 80°C destroys the ability of the carbon to adsorb gold cyanide.
- (6) The neutral complex $\text{Hg}(\text{CN})_2$ competes directly

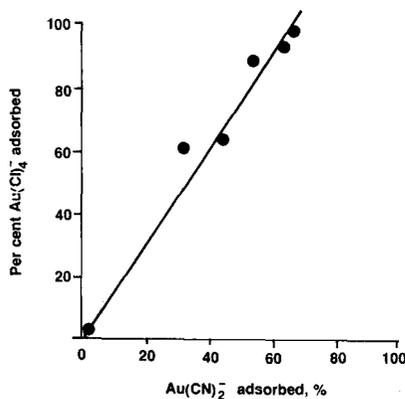


Fig. 12—The amount of gold adsorbed from a solution containing initially 800 mg of gold per litre dissolved as $\text{Au}(\text{Cl})_4^-$ (adjusted to pH 1 with HCl) versus the amount of gold cyanide adsorbed from a solution containing initially 250 mg of gold per litre dissolved as $\text{KAu}(\text{CN})_2$ on various coconut-shell carbons that differ in their reducing power

TABLE V
ADSORPTION OF $\text{Au}(\text{CN})_2^-$ AND $\text{Au}(\text{Cl})_4^-$ ON CHLORINE-DEACTIVATED CARBON*

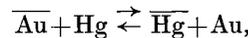
Composition of adsorption medium	Gold adsorbed on 0,25 g of carbon	
	Carbon (chlorine) mg	Carbon mg
600 mg.l ⁻¹ Au as $\text{Au}(\text{CN})_2^-$ + 10^{-2} M HNO_3	10	29
600 mg.l ⁻¹ Au as $\text{Au}(\text{CN})_2^-$ + 8×10^{-2} M CaCl_2	10,5	26
250 mg.l ⁻¹ Au as $\text{Au}(\text{CN})_2^-$	5	9
1 000 mg.l ⁻¹ Au as $\text{Au}(\text{Cl})_4^-$ + 10^{-1} M HCl	22	50

* The tests were done by the batch technique, and 0,25 g of carbon and 50 ml of solution were used. To oxidize the carbon, 2) g of carbon was placed in 100 ml of water and Cl_2 was bubbled into the water for 2 days.

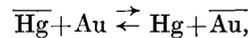
with $\text{Au}(\text{CN})_2^-$ for adsorption sites, and can even displace some of the adsorbed gold from activated carbon. This suggests very strongly that the negative charge is not essential for adsorption by activated carbon. The data in Table VI were used in equation (9) for the calculation of the distribution coefficient $K \text{ Au/Hg}$ for the $\text{Au}(\text{CN})_2^-/\text{Hg}(\text{CN})_2$ system:

$$K \text{ Au/Hg} = \frac{[\overline{\text{Au}}] [\text{Hg}]}{[\text{Au}] [\overline{\text{Hg}}]} \dots \dots \dots (9)$$

In equation (9), $\overline{\text{Au}}$ and $\overline{\text{Hg}}$ represent the relevant metal adsorbed on the carbon, and Au and Hg the effective concentrations in solution. For the adsorption reaction,



(i.e., for carbon that initially held gold and was then re-equilibrated for a period of 24 hours with $\text{Hg}(\text{CN})_2$ only) the average value of $K \text{ Au/Hg}$ was found to be 12,5, whereas, for the reverse adsorption process,



the average value of $K \text{ Au/Hg}$ was found to be 3,5. The large discrepancy between $K \text{ Au/Hg}$ for the forward and reverse adsorptions indicates that the adsorption process is not completely reversible, and therefore the value of $K \text{ Au/Hg}$ depends on which species is initially present on the carbon. Therefore, if $\text{Au}(\text{CN})_2^-$ and $\text{Hg}(\text{CN})_2$ are simultaneously adsorbed on carbon from the same solution, the value of $K \text{ Au/Hg}$ would be expected to fall between 3,5 and 12,5, since the two species, which adsorb at similar rates, are competing directly for adsorption sites. The value calculated from experimental data is 10.

The Nature of the Gold Cyanide Adsorbate

Although the exact identity of the gold adsorbate has not been established, the results of this investigation lead to the following deductions about its nature.

The adsorption of neutral molecules on carbon (e.g., $\text{Hg}(\text{CN})_2$, a covalent compound) is not influenced by the ionic strength or acidity of the adsorption medium (see Fig. 13), whereas the adsorption of anions usually shows a marked dependence on both these factors. However, as mentioned above, the neutral $\text{Hg}(\text{CN})_2$ and anionic $\text{Au}(\text{CN})_2^-$ compete for the same sites on the carbon, which indicates that the ionicity of the anion is not essential for adsorption. According to Traube's rule²⁶, the distribution coefficients for the adsorption of a homologous series of organic compounds onto carbon closely follows the order of solubility of the various members of the series in the adsorption medium. Lower solubility leads to higher distribution coefficients on carbon. The mechanism of the ionic-strength effect presumably involves a lowering of the solubility of the anionic species $\text{Au}(\text{CN})_2^-$ in the aqueous phase, thereby accounting for the higher loading observed in the presence of added electrolytes and acids. It is not clear at this stage whether the compounds of lower solubility are loaded by physical adsorption onto the carbon surface, or whether they are deposited as microcrystal-

TABLE VI

AMOUNT OF METAL DISPLACED AND ADSORBED AFTER EQUILIBRATION WITH METAL CYANIDE COMPLEX

Initial metal content per 0,25g of carbon mg	Initial metal content per 50 ml of solution mg	Amount of metal displaced from carbon per 50 ml of solution mg	Amount of metal adsorbed by carbon per 0,25 g of carbon mg
Au 30,3	Hg 37,0	Au 2,6	Hg 15,0
Au 32,8	Hg 42,5	Au 3,3	Hg 17,5
Au 33,8	Hg 47,5	Au 4,3	Hg 18,0
Au 36,5	Hg 53,0	Au 4,8	Hg 20,5
Hg 26,0	Au 33,8	Hg 13,5	Au 27,6
Hg 29,5	Au 39,3	Hg 14,5	Au 31,0
Hg 33,0	Au 43,8	Hg 15,5	Au 32,9
Hg 34,5	Au 46,5	Hg 17,5	Au 33,5

lites in a manner similar to the capillary condensation of molecules from the gas phase. As an empirical observation, the solubility rule provides a useful guide to orders of strength of adsorption. In the case of $\text{Au}(\text{CN})_2^-$, however, it appears that these cation effects are simply an effect over and above the basic mechanism.

The suggestion that the aurocyanide ion is reduced to metal on the surface of the activated carbon can also be discounted as a mechanism of adsorption by a consideration of the results of the reduction potential measurements (Fig. 11). Thus, the most negative value of the potential recorded in Fig. 11 ($-0,14\text{V}$) versus the saturated calomel electrode (SCE) is considerably more positive than the standard reduction potential for $\text{Au}(\text{CN})_2^-$ ($-0,85\text{V}$), and reduction to the metal is therefore unlikely. However, from chloride solutions ($E^0 = +0,80\text{V}$ vs SCE) reduction is possible and is observed. It is interesting to note that, even at relatively low gold loadings, metallic gold is visible on the surface of the carbon after it has been exposed to a solution of $\text{Au}(\text{Cl})_4^-$ ions. No such gold is visible even at high gold loadings from cyanide solutions. This implies, and

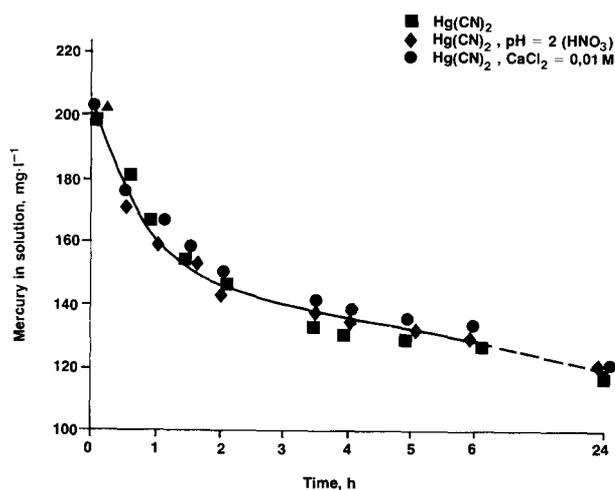


Fig. 13—Effect of 10^{-2} M HNO_3 and 10^{-1} M CaCl_2 on the rate of adsorption of $\text{Hg}(\text{CN})_2$ on carbon (experimental conditions: volume of solution 300 ml, mass of carbon 0,25 g, nitrogen atmosphere, initial concentration of mercury 205 mg.l^{-1})

electron-microscope scans of a cross-section of a loaded particle have confirmed, that the gold species is adsorbed within the pores of the particle. This means that reduction does not occur by the transfer of electrons through the solid to the surface, as it apparently does in the case of reduction from chloride solutions.

The implication is that the presence of pores or a surface on which adsorption can occur is necessary for adsorption of the aurocyanide ion. The reduction of the aurocyanide anion on carbon, as indicated by XPS, could be accounted for in two ways.

(i) It is well known that the deposition of a metal onto a foreign metal substrate often occurs at potentials positive to the thermodynamic potential for such processes. This 'underpotential' deposition arises from the interaction of the deposited metal ad-atoms with the substrate. Measurements of the electroadsorption valency have indicated that, because of this (often strong) interaction, the first monolayer of deposited metal has an effective oxidation state that is intermediate to that of the ion and the metal. It is suggested that this could occur during the adsorption of aurocyanide ions. In addition, charge-transfer adsorption could be facilitated by the well known property of $\text{Au}(\text{I})$ to form linear chains with CN^- acting as a bridging group³⁵. The strong adsorption of $(\text{AuCN})_x$ on gold electrodes, and more recently the electrochemical irreversibility of the deposition of gold from cyanide solutions, have been proposed as a mechanism for the passivation of gold in cyanide solutions.

(ii) The second possibility relates to the presence on the carbon of cluster compounds of gold. Cluster compounds³⁴ of the type $[\text{Au}_{11}(\text{CN})_3L_7]$ where $L = \text{P}(\text{C}_6\text{H}_5)_3$ can be obtained by the reduction of $L\text{AuCN}$ with sodium borohydride or potassium hydroxide in alcohol. The XPS spectra of these compounds have been used to give structural information on the clusters. For example, the $[\text{Au}_{11}(\text{CN})_3L_7]$ cluster is believed to be a pentagonal bipyramid composed of three $\text{Au}(\text{I})$ and eight $\text{Au}(\text{0})$ atoms. However, the interesting feature of the XPS spectrum of this compound is that, although the cluster formally contains gold in both the $\text{Au}(\text{0})$ and $\text{Au}(\text{I})$ oxidation states, the spectrum

shows a single $4f_{7/2}$ gold band similar in form to that present in mononuclear gold compounds. This implies that the gold atoms all have very similar charge densities, and this has been ascribed to a strong electron delocalization over the entire coordination polyhedron. Therefore, the binding energy of the $4f_{7/2}$ photoemission band falls somewhere between the binding energy of $\text{Au}(\text{0})$ and that of $\text{Au}(\text{I})$ mononuclear compounds.

The XPS spectra obtained for the carbons that are loaded with gold are similar to those obtained for cluster compounds of gold in that the minimum between the $4f_{5/2}$ and $4f_{7/2}$ photoemission bands is not as low as that shown by the individual mono-

nuclear gold compounds and Au(0) (see Fig. 9). An interesting generalization³⁶ about the cluster compounds of gold obtained so far is that they are all neutral compounds or cations that contain six, nine, or eleven gold atoms in which the average oxidation state of the gold varies between 0,2 and 0,33.

Furthermore, the clusters are generally highly insoluble in water³⁷. Since it is well known that, if two species are competing for adsorption on carbon, the species that is least soluble in the adsorption medium is adsorbed preferentially on the carbon, the strong adsorption of gold on carbon from cyanide solution can be rationalized in terms of the adsorption of a cluster compound of gold.

CONCLUSIONS

The mechanism of adsorption of aurocyanide on carbon appears to involve adsorption of the aurocyanide as the less soluble $M^{n+}[\text{Au}(\text{CN})_2]_n$ complex ($M = \text{Na}^+$, K^+ , Ca^{2+} , H^+), which probably accounts for the initial adsorption stage, followed by a reduction step in which either a sub-stoichiometric $\text{AuCN}(x)$ surface species or a cluster-type compound of gold is formed. Experiments are now in progress that, it is hoped, will clarify the exact mechanism of adsorption.

ACKNOWLEDGEMENT

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