THE INDUCED EXCHANGE OF Cl⁻ AND AuCl₄⁻. EVIDENCE FOR Au(II)

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The reduction of AuCl₄⁻ by Fe⁺⁺ induces a rapid exchange of Cl⁻ and AuCl₄⁻. Under the conditions studied a turnover of Cl⁻ per Fe⁺⁺ of the order of 10⁴ has been observed. Sn(II) and Sb(III), though oxidized by AuCl₄⁻, are much less efficient inducing agents, and may in fact have no direct effect. Au(I) induces, at most, only a slow exchange. V(IV) is fairly effective, but its efficiency is diminished by accumulation of V(V). It is concluded that a form of Au(II) is the active catalyst. This is generated efficiently by one-electron reducing agents, but not by the agents Sn(II) and Sb(III), which apparently bypass Au(II) in reducing AuCl₄⁻. The kinetics of the reaction induced by Fe⁺⁺ are consistent with a mech-anism in which Au(II) is generated by a second-order reaction of AuCl₄⁻ and Fe⁺⁺ (specific rate, k_1), Au(II) exchanges associated chloride very rapidly with Cl⁻, undergoes rate-determining exchange with Au(III) (k_3), and is destroyed by dis-proportionation (k_4). The specific rate k_1 was measured as 1.8 × 10⁴ l. mole⁻¹ min.⁻¹, and lower limits of 10⁸ and 10¹⁰ l. mole⁻¹ min.⁻¹ have been set on k_3 and k_4 . all at 0[°]. mole⁻¹ min.⁻¹ have been set on k_3 and k_4 , all at 0°.

Introduction

In a separate article,² the rate characteristics of the spontaneous exchange of $AuCl_4^-$ and Cl^- are described. Observations made in the course of that work, on the exchange induced by an unknown impurity in ordinary distilled water, led to an investigation of the exchange induced by various reducing agents, and exposed the extraordinary sensitivity of the system to certain reducing agents. notably Fe⁺⁺. This paper describes the results of exploratory experiments with a variety of reducing agents, as well as results of a more detailed kinetic study made with Fe⁺⁺.

Reagents.—Many of the reagents are the same as de-scribed in the previous paper. The others were prepared from the purest available reagents and redistilled water as follows, the concentrations being calculated from the amounts of reagents used.

Solutions of $K_4Fe(CN)_8$, $3H_2O$, $K_3Fe(CN)_6$, HVO_3 (from V_2O_5), $KSbOC_4H_4O_6$, $NaKC_4H_4O_6$ and KCN were prepared directly. The hexacyanoferrate solutions were freshly pre-

are before use. The NaClO₂ was recrystallized before being used. Solutions of $Fe(o-phen)_3SO_4$ were prepared by dissolving nearly equivalent quantities of $Fe(NH_4)_2(SO_4)_2.6H_2O$ and

1:1 of phenanthroline in water. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (hereafter implied where FeSO₄ is written), $Fe(NO_3)_3 \cdot 9H_2O$ and $SnCl_2 \cdot 2H_2O$ were dissolved in dilute solutions of sulfuric, perchloric and sulfuric acids, re-spectively, to decrease oxidation or hydrolysis. The ferrous and stannous solutions were freshly prepared before

rous and standous solutions were freshly prepared before use. A part of the ferrous solution was always diluted to the final strength immediately before being used. For most of the experiments with V(IV), (able I), C.P. VOSO₄ was weighed out quickly and dissolved. For the other experiments a solution was prepared as follows: A mixture containing 9.106 g, of V₂O₅, 20 ml. of concd. H₂SO₄ and some water was warmed and treated with SO₄ gas until and some water was warmed and treated with SO2 gas until half an hour after all the V₂O₅ had dissolved. Nitrogen was passed through the solution on the steam-bath overnight and the solution was filtered and diluted to 100 ml. of 1.00 f VOSO₄, 3.1 f H₂SO₄.

Experimental Procedure.-The procedure was usually as described in the previous paper except that the catalyst and or inhibitor (included in the 4 ml. total volume during ex-change unless otherwise specified) was first added sometimes to the chloroaurate and sometimes to the radioactive solu-tion in the divided flask.

Definitions and Derivations

This section contains derivations of the equations for the exchange induced by the reaction of Fe++ with AuCl₄-, based on the mechanism presented in the discussion. A system of this type

- (1) Atomic Energy Commission Predoctoral Fellow.
- (2) R. L. Rich and H. Taube, THIS JOURNAL, 58, 1 (1954).

differs from that ordinarily discussed in which R, the rate of the reaction carrying the exchange, is constant. Here R decreases with time, since the inducing agent is consumed during the time of the exchange.

Let $\overline{F} \equiv (\text{Fe}^{++}), A \equiv (\text{Au}(\text{III})), G \equiv (\text{Au}(\text{II})),$ $b \equiv$ equivalent concentration of complexed chloride \equiv (Cl_c) + (Cl_c*) = 4A, $a \equiv$ (Cl⁻) + (Cl*⁻), $C \equiv$ (Cl_c*) + (Cl*⁻), $x \equiv$ (Cl_c*), $y \equiv$ (Cl*⁻), $n \equiv$ the number of chlorides changing association from Au(II) to Au(III) as a result of each exchange between the latter. Probably n = 3 or 4. Also let ϕ $= (y - y_{eq})/(y_0 - y_{eq})$ and $\theta = (y - y_{eq})/(y_i - y_{eq})$. The subscript 0 refers to initial conditions, eq. to complete isotope equilibrium (infinite time for all paths), f to completion of the ferrous-induced exchange (infinite time for this path alone).

Assuming, for ferrous-induced exchange, the mechanism proposed in this paper (see Discussion), we can abbreviate the rates for steps 1, 3 and 4. respectively, as k_1AF , k_3AG and k_4G^2 .

Set $A_0 \gg F_0$ (actually $3.2 \times 10^2 < (A_0/F_0) < 5.2 \times 10^4$). Then

$$\frac{\mathrm{d}F}{\mathrm{d}t} = -k_1 A_0 F \text{ and } F = F_0 e^{-k_1 A_0 t} \tag{I}$$

$$\frac{\mathrm{d}G}{\mathrm{d}t} = k_1 A_0 F - k_4 G^2 = k_1 A_0 F_0 e^{-k_1 A_0 t} - k_4 G^2$$

Assume a steady state is quickly reached, *i.e.*, $dG/dt \approx 0$. Then

$$G = \sqrt{\frac{k_1 A_0 F_0}{k_4}} e^{-1/2(k_1 A_0 t)}$$

$$\frac{dy}{dt} = -nk_3 A_0 G \left(\frac{y}{a} - \frac{x}{b}\right) \qquad (II)$$

$$= -nk_3 A_0 G \left(\frac{y}{a} + \frac{y}{b} - \frac{c}{b}\right)$$

$$I) = c \overline{A_0} = \sqrt{\frac{k_1 A_0 F_0}{k_1 A_0 F_0}}$$

$$dy \Big/ \Big[\Big(\frac{1}{a} + \frac{1}{b} \Big) y - \frac{c}{b} \Big] = -nk_3 A_0 \sqrt{\frac{k_1 A_0 F_0}{k_4}} e^{-1/2(k_1 A_0 t)} dt$$

$$\frac{ab}{k_4} \ln \left(\Big(\frac{1}{a} + \frac{1}{b} \Big) y - \frac{c}{b} \Big) = 2nk_{34} \sqrt{\frac{A_0 F_0}{k_4}} e^{-1/2k_1 A_0 t} + \text{Const.}$$

 $\overline{a+b}$ In $\left(\left(\overline{a}+\overline{b}\right)^y-\overline{b}\right)=2mn_3\sqrt{k_1k_4}$

In our experiments $y_0 = c$, therefore Const. = (ab/ $(a + b) \ln(c/a) - 2nk_3 \sqrt{A_0 F_0/k_1 k_4}$

$$\ln\left(\frac{a+b}{ab}y - \frac{c}{b}\right) = \ln\frac{c}{a} - \frac{a+b}{ab}2nk_3\sqrt{\frac{A_0F_0}{k_1k_4}}\left(1 - e^{-1/2(k_1A_0t)}\right) \quad \text{(III)}$$

Since $b = 4A_0$ we define

$$\frac{a+b}{2a}nk_{3}\sqrt{\frac{F_{0}}{k_{1}k_{4}A_{0}}}\left(1-e^{-1/2^{(k_{1}A_{0}t)}}\right) \equiv \alpha$$

then

$$\frac{a+b}{ab} y - \frac{c}{b} = \frac{c}{a} e^{-\alpha} \text{ and } y = \frac{c}{a+b}(a+b e^{-\alpha})$$

In any case $y_{eq} = (a/a + b)c$ necessarily. $y - y_{eq} = (bc/a + b)e^{-\alpha}$.

$$y_0 - y_{eq} = c - \frac{ac}{a+b} = \frac{bc}{a+b}$$
$$\phi \equiv \frac{y - y_{eq}}{y_b - y_c} = e^{-\alpha} \qquad (IV)$$

Let $t \rightarrow \infty$ (only induced exchange occurring), then

$$\alpha_{\rm f} \equiv (a + b/2a) nk_3 \sqrt{F_0/k_1 k_4 A_0} \tag{V}$$

and

$$\phi_t \equiv \frac{y_t - y_{eq}}{y_0 - y_{eq}} \tag{VI}$$

We see that $\alpha/\alpha_f = 1 - e^{-1/2(k_iA_0t)}$. Treatment of Data at Finite *t*.

$$\frac{1}{2}(k_1A_0t) = -\ln\left(1 - \frac{\alpha}{\alpha_t}\right) = \ln\alpha_t - \ln(\alpha_t - \alpha) = \\ \ln\alpha_t - \ln\ln\frac{\phi}{\phi_t} = \ln\alpha_t - \ln\ln\frac{y - y_{eq}}{y_t - y_{eq}} \equiv \ln\alpha_t - \\ \ln\ln\theta = (\ln\alpha_t - \ln\ln10) - \ln\log\theta$$

Or

$$\ln \log \theta = \text{const.} - 1/2(k_1 A_0 t)$$
(VII)

Limitations Implied by the Steady State Assumption.—The assumption $dG/dt \approx 0$ implies $|dG/dt| \ll k_1 A_0 F_0 e^{-K_1 A_0 t} \approx k_4 G^2$.

Since

$$G \approx \sqrt{\frac{k_1 A_0 \overline{F}_0}{k_4}} e^{-1/2(k_1 A_0 t)}$$

1/2(k_1 A_0) $\sqrt{\frac{k_1 A_0 \overline{F}_0}{k_4}} e^{-1/2(k_2 A_0 t)} \ll k_1 A_0 \overline{F}_0 e^{-k_1 A_0 t}$ (VIII)

The exchange depends on $e^{-1/2(k_1A_0t)}$. The linearity of Fig. 1 suggests the validity of the inequality at least until $e^{-1/2(k_1A_0t)}$ becomes less than 0.1 for all points on the graph. Therefore $1/2(k_1A_0)$ $\sqrt{k_1A_0F_0/k_4} < 0.1k_1A_0F_0$ and $(k_1/k_4) < (F_0/25A_0)$. For Fig. 1 the smallest experimental F_0/A_0 is 6.9×10^{-5} and $k_4/k_1 > 3.6 \times 10^5$ (IX)

Exploratory Experiments.—In Table I the total volume of solution was usually 4.25 ml. The 0.25 ml. of catalytic solution was added to the side of the divided flask containing radioactive chloride except where indicated otherwise. The temperature during the exchange in these and other experiments was always 0.0°. Concentrations of the inducing agent, etc., are given for the final mixed solution. Other final conditions, except where indicated otherwise, were: $(AuCl_4^-) = 0.00584 \ f, (Cl^-) = 0.0154 \ f, (H^+) = 0.069 \ f,$ ionic strength $\mu = 0.088$ neglecting the varying small catalyst concentrations. Under these conditions the expected half-time for the uncatalyzed exchange is 2.96 minutes so that in 10 seconds we should have 4% exchange and in 30 seconds 11%. The tabulated data are uncorrected.

The % exchange is defined as: % ex. $\equiv 100$



Fig. 1.—Exchange induced by vanadyl. Conditions as in exp. 1.14 of the previous paper with addition of 2.5×10^{-5} VOSO₄.

 $(1 - \phi) \equiv 100(y_0 - y/y_0 - y_{eq})$ where y_0 was chosen to include the effect of the catalyst in the water.

A short spectrophotometric study (see Discussion) was made of a solution which initially contained 0.00763 f RbAuCl₄, 0.00077 f KSbOC₄H₄O₆, 0.00077 f HCl, 0.0183 f NaCl, 0.088 f HNO3 and 0.0019 f NaKC₄H₄O₆. The temperature was about 26°. The optical density at 4600 Å. varied as shown in Table II. The difference between the first and last values is that expected if the yellow $AuCl_4^-$ was reduced to the colorless $AuCl_2^-$ since the antimony was equivalent to one-tenth of the gold. The following day gold flakes appeared and the optical density rose gradually to 0.359, or higher when stirred. When excess antimony(III) was added to a similar solution the mixture eventually became colorless and much later also deposited gold flakes.

Ferrous Induced Reaction.—Table III shows the results of a study of the exchange induced by ferrous ion. The significance of the entries in the last two columns is dealt with in the Discussion section.

Discussion

Experiments 1.11–1.15 show that Fe^{++} is very efficient in inducing the exchange of $AuCl_4^-$ and Cl^- ; thus $6 \times 10^{-7} M$ FeSO₄ carries a solution $6 \times 10^{-3} M$ in $AuCl_4^-$ and $15.4 \times 10^{-3} M$ in $Cl^$ about 50% of the way to exchange equilibrium. The effect of Fe⁺⁺ under the conditions of experiments 1.14 and 1.15 is essentially complete after 5 sec. Sn(II)- and Sb(III)-tartrate are fairly rapidly oxidized by $AuCl_4^-$. These substances are, however, much less effective in inducing the exchange than is Fe⁺⁺. The experiments performed with Sb(III) (1.31 to 1.35) afford a definite conclusion as to the oxidation state of Au (in the active catalyst) formed by the inducing agent. The change of optical density with time observed in the reaction of excess $AuCl_4^-$ with Sb(III) (cf. Table II) shows that formation of Au(I) is the primary net change, and that this stage is complete

No.	$\frac{10^4 \times \text{concn.}}{\text{Catalyst}}$	(f)	Other	Time,	% ex.	Misc.
1.11	0.06 FeSO_4	15	Fe(NO ₃) ₃	10.1	90	
1.12	0.06 FeSO4			9.6	87	$0.078 \text{ H}^+, \mu = 0.106$
1.13	0.006 FeSO ₄			10.0	53	<i>,</i> , ,
1.14	0.006 FeSO_4			5.1	52	
1.15	0.006 FeSO ₄			10.0	51	0.018 H+
1.21	$0.1 \ \mathrm{SnCl}_2$			9.5	8	
1.31	6 KSbOC ₄ H ₄ O ₆	15	NaKC4H4O6	9.7	34	
1.32		30	NaKC4H4O6	9.6	26	
1.33	$6 \text{ KSbOC}_4\text{H}_4\text{O}_6$	15	$NaKC_4H_4O_6$	9.5	16	Cat. in AuCl ₄ -3 hr. at 29°
1.34	$6 \text{ KSbOC}_4 H_4 O_6$	1.	5 NaKC4H4O6	10.0	18	Cat. in AuCl ₄ -3 hr. at 29°
1.35	Same as 1.34 ± 0.2 FeSO ₄			10.1	98	Tart. alone in AuCl ₄ - 2 hr. at 29°
1.36	Same as 1.35			10.1	97	(Cat. mixture all in HCl*)
1.41	1 VOSO4			10.4	28	
1.42	1 VOSO4			10.0	46	0.018 H+
1.43	1 VOSO_4			29.7	ca. 58	
1.44	1 VOSO ₄	1	HVO_3	29.6	32	
1.45	1 VOSO_4			29.7	30	Cat. in AuCl ₄ ^{$-$} during 15' cooling
1.51	0.25 VOSO ₄			5.0	18ª)	$(0.00620 \text{ AuCl}_4^-,$
1.52	$.064 \text{ FeSO}_4$			4.9	85 }	{ 0.0163 Cl ⁻ , 0.0667 H+
1.53	$.064 \text{ FeSO}_4 + 0.25 \text{ VOSO}_4$			5.0	78)	pure VO ⁺⁺ , 4 ml. vol.
1.61	$.07 \text{ K}_{4} \text{Fe}(\text{CN})_{6}$			3.4	27	
1.62	.07 K ₄ Fe(CN) ₆			9.9	52°	
1.63	$.08 \text{ K}_4 \text{Fe}(\text{CN})_6 + 2.5 \text{ K}_3 \text{Fe}$	$(CN)_6$		10.1	43	
1.64	$25 \times \text{conen. of } 1.63$			9.6	-12	$\mu = 0.126$
1.65	Same as 1.63			9.4	54	0.018 H ⁺
1.71	$0.6 \text{ Fe}(o-\text{phen})_3 SO_4$			9.8	100	Slight excess $FeSO_4$
1.72	$0.6 \text{ Fe}(o-\text{phen})_3 SO_4$			10.4	ca. 0	Slight excess o-phen.
1.81	5 NaClO ₂			10.3	3	
۵ Esti	mated from Fig. 1.					

TABLE I

EFFECT OF VARIOUS SUBSTANCES IN INDUCING THE EXCHANGE OF AUCL⁴ WITH Cl⁻

TABLE II

	REACTION OF Sb	(III) with AuCl	4-
<i>t</i> , min.	Density	<i>t</i> , min.	Density
0.4	0.362	27.5	0.3425
1.4	.360	29.0	.3415
3.0	.358	39	. 3365
6.0	.355	50	.334
12.5	.350	70	.331
18.0	.348	110	. 326
23.0	.345		

still is active in a solution such as was prepared for experiment 1.34, it cannot be argued that Au(I) is the active agent but that its effect is suppressed by some other component of the solution. The slight induced exchanges observed in experiments 1.33 and 1.34 can be attributed to the effects of tartrate (cf. exp. 1.32) and probably of Au(I) in generating the catalyst. The conclusion seems unavoidable that this catalyst is Au in the oxidation state +2, and that it is generated efficiently by

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TABLE III

(INETICS OF T	EXCHANGE	INDUCED 1	вү Fe
(INETICS OF T	EXCHANGE	INDUCED 1	ву Fe

(۵	000	\overline{T}	- 0	٥°	4	_	5	800	١
(11. ==	U	USS.	1	= ()	. U *.	L	=	D.	sec.	1

$(\mu = 0.000, 1$	-0.0,0-0	BC0.)		
. ,	3.1	3.2	3.3	3.4
(Cl ⁻)	0.01718	0.01655	0.01624	0.00664
(AuCl ₄) ₀	0.01240	0.00620	0.00310	0.00620
$(Cl^{-}) + (Cl_{c})$	0.0668	0.0414	0.0286	0.0314
(H^+)	0.0609	0.0667	0.0701	0.0690
$[(\mathrm{Cl}^{-}) + (\mathrm{Cl}_{\circ})] / [(\mathrm{Cl}^{-}) \sqrt{(\mathrm{Au}\mathrm{Cl}_{4})_{\circ}}]$	34.9	31.7	31.7	60.1
$-\Delta \ln \phi_t / \Delta \sqrt{(Fe^{++})_0}$	864 ± 40	750 ± 7	656 ± 70	1310 ± 20
$-[\Delta \ln \phi_{\rm f}/\Delta ({\rm Fe^{++}})_0]/[({\rm Cl^-}) + ({\rm Cl_c})/({\rm Cl^-})\sqrt{({\rm AuCl_4^-})_0]}$	24 .7	23.6	20.7	21.8

after 2 hours. Eventually $AuCl_4^-$ is partially restored and Au is formed by the disproportionation reaction 3Au(I) = Au(III) + 2Au. Au(I) was pre-formed in experiments 1.33 to 1.34 using Sb(III) as the reducing agent. The comparison of the exchange results in these experiments with those obtained using Fe⁺⁺ as the inducing agent shows that Au(I) is not the active catalyst. Since Fe⁺⁺ Fe⁺⁺, but much less efficiently by the $2e^{-}$ reducing agents Sn(II) and Sb(III).

The experiments with the one-electron reducing agent VO⁺⁺ provide further support for the conclusions. Although VO⁺⁺ is oxidized only very slightly, it is a fairly effective inducing agent. Because of the low rate of oxidation of VO⁺⁺ by AuCl₄⁻, the system seemed a promising one for a Jan. 1954

thorough kinetic study but it proved disappointing in this respect. Figure 1, in which the exchange induced by VO++ is displayed as a function of time, shows that its efficiency decreases markedly as time progresses. This decline is not due to net consumption of VO^{++} which can be only very slight, and is apparently due to the accumulation of V(V). Such an effect for V(V), operating by reversal of the reaction, Au(III) + V(IV) =Au(II) + V(V), is not surprising for a couple as weakly reducing as V(IV)-V(V). This interpretation of the cause of the decline is supported by the increased inducing effect of V(IV) at lower acidity (exp. 1.42 compared to 1.41), by the observed inhibitory effect of HVO₈ (exp. 1.44 compared to 1.43), and by the decrease in the effi-ciency of VO^{++} when it is left in contact with AuCl₄⁻ before radioactive chloride is added (exp. 1.45 compared to 1.43). V(V) freshly formed by oxidation of VO⁺⁺ is much more effective than HVO₃ prepared as outlined in the experimental part. Its efficiency depends on its history and is improved by heating in dilute solution. These complexities presumably are due to slow condensation equilibria involving V(V), and because of them, a more detailed kinetic study was not undertaken. Experiments 1.51, 1.52 and 1.53 show that a mixture of V(IV) and Fe^{++} induces less exchange than would be expected for the substances acting independently, and in fact less than does Fe⁺⁺ alone. The result suggests that VO^{++} , being left at high concentration, partially destroys Au(II), reducing it to Au(I).

Although ClO_2^- can function as a one-electron reducing agent, it is entirely without effect as an inducing agent. The value of E^0 for $\text{ClO}_2^--\text{ClO}_2$ is -1.2 v., and ClO_2^- may be too weak as a reducing agent to generate Au(II) at sufficiently high concentration.

The kinetic data obtained with Fe⁺⁺ as inducing agent support the conclusion that Au(II) is the catalyst. The observations recorded in Table I show that the inhibition by Fe⁺⁺⁺ formed in the reaction can only be very slight, and that a fourfold change in acidity is also without effect. It will be convenient to discuss the data of Table III on the variation of the induced exchange with concentration of Fe⁺⁺, Cl⁻ and AuCl₄⁻, referring to the following mechanism for the mode of action of Au(II).

$$Fe^{++} + AuCl_4^{-} \longrightarrow Fe(III) + K_1(Fe^{++})(AuCl_4^{-}) \quad (1)$$

$$Au_{Ci^{-}}^{II} + Cl^{*} = Au_{Cl^{*-}}^{II} + Cl^{-} \quad \text{Very rapid} \qquad (2)$$
$$Au_{Cl^{+}}^{II} + Au_{Cl^{+}}^{II} + Au_{Cl^{+$$

$$AuCl_4^{*-} \quad k_3(Au(II))(AuCl_4^{-}) \quad (3)$$

2Au(II) \longrightarrow Au(I) + Au(III) $\qquad k_4(Au(II))^2 \quad (4)$

If the chains are long (as is certainly true since the turnover of Cl^- is very large compared to the amount of Fe⁺⁺ consumed), the mechanism leads (see equations) to the rate law

$$\ln \frac{(\mathrm{Cl}^{*-}) - (\mathrm{Cl}^{*-})_{\mathrm{eq}}}{(\mathrm{Cl}^{*-})_{0} - (\mathrm{Cl}^{*-})_{\mathrm{eq}}} \equiv \ln \phi = -\frac{(\mathrm{Cl}^{-}) + (\mathrm{Cl}_{\mathrm{e}})}{2(\mathrm{Cl}^{-})} n k_{3} \sqrt{\frac{(\mathrm{Fe}^{++})_{0}}{k_{1} k_{4} (\mathrm{AuCl}_{4})_{0}}} (1 - e^{-1/2^{k_{1}}(\mathrm{AuCl}_{4}^{-})_{0}t})$$

where (Cl^{-}) and (Cl_{c}) now represent the total concentrations of free chloride and complexed chloride and n is 3 or 4. The entries for each row in Table III were obtained by measuring the total exchange induced by Fe^{++} acting for 5 seconds, using various initial concentrations of Fe⁺⁺ at fixed values of $(AuCl_4^-)$, (Cl^-) and (H^+) as shown in Fig. 2. The consumption of Fe⁺⁺ is sufficiently complete in 5 seconds, except at the lowest concentration of AuCl₄⁻, so that the term $(1 - e^{-\frac{1}{2}k_1(AuCl_4-o_t)})$ is essentially equal to unity, with the one exception. Figure 2 shows the variation of $\ln \phi_t$ (f implies $t \to \infty$) with $\sqrt{(\text{Fe}^{++})_0}$ for exp. 3.2. The relation demanded by the mechanism is followed strictly, and the line through the points covering a 15-fold range in $(Fe^{++})_0$ extrapolates well at $(Fe^{++}) = 0$ to the spontaneous exchange expected in five seconds. Similar data provided the bases for other entries in column 7 of Table III. The figures in the last column of Table III should be a constant if the proposed mechanism accounts also for the influence on the induced exchange of varying the concentration of $AuCl_4^-$ and Cl^- . The agreement of the values, with some apology for the experiment at lowest AuCl₄-, is satisfactory.



Fig. 2.—Induced exchange as a function of square root of ferrous concentration, exp. 3.2.

It should be noted that the data do not establish the formula of the catalyst Au^{II}_{Cl}-. On this point they require merely that the rate-determining reaction 3 and the disproportionation reaction 4 in combination do not introduce dependence on chloride ion concentration. Reasonable formulations for the catalyst would appear to be AuCl₄⁻ or AuCl₃⁻. On the former assumption, reaction 3 becomes an electron transfer process; on the latter, it requires transfer of Cl. In any event, it seems likely that the very great lability of Au^{II}Cl⁻ as compared to AuCl₄ is due to the possibility of states of different coördination number for Au(II) having nearly the same energy. The electronic structures for AuCl₄= and AuCl₃⁻ can be represented as DSPPp' and DSPp'. Some compensation in energy for the loss of Cl^- is expected from the increase in average stability of the hybridized orbitals, from increase in stability of the electron in the atomic orbital,

and from the decrease in repulsion of negative ions. The phenomenon of an intermediate oxidation state having extraordinary lability with respect to substitution is not unique for Au, but appears to be the explanation for some induced exchanges observed with $PtCl_{6}$ (to be published), with $Pt^{III}Cl^{-}$ being much more labile than $PtCl_{4}$ or $PtCl_{6}$.

Equations III and VIII show that by measuring the induced exchange at times short enough so that the consumption of Fe⁺⁺ is not complete, it is possible to obtain the value of k_1 . An attempt to do this has been made. Low chloroaurate concentration was chosen to prolong the life of the inducing agents. Its concentration and that of H⁺ and Cl⁻ were the same as in experiment 3.3. The initial concentration of Fe⁺⁺ was 2.43 $\times 10^{-6} f$. The relation pertinent to these results is equation (VII)

$$\ln \log \theta \equiv \ln \log \frac{(\mathrm{Cl}^{*-}) - (\mathrm{Cl}^{*-})_{\mathrm{eq}}}{(\mathrm{Cl}^{*-})_{\mathrm{f}} - (\mathrm{Cl}^{*-})_{\mathrm{eq}}} = \operatorname{const.}_{\mathrm{const.}} - \frac{1}{2k_{\mathrm{f}}}(\mathrm{AuCl}_{\mathrm{f}})_{\mathrm{o}t}$$

Figure 3 shows a logarithmic plot of log θ vs. t. From the slope of the line, taking account of the concentration of AuCl₄-, k_1 is found to be 1.8 × 10⁴ l. mole⁻¹ min.⁻¹. It can be seen that the halftime for log θ is 1.5 sec., and that of the controlling oxidation-reduction reaction is 0.75 sec. The measured value of k_1 combined with the average value of the function in the last column of Table III yields, using eq. V and VI, for nk_3/k_4 the value $6 \times 10^3 l.^{1/2}$ mole^{-1/2} min.^{-1/2}. The experimental results provide no basis for making accurate estimates of k_3 or k_4 separately. Only lower limits can be set. Using inequality (IX) and our value of k_1 we find $k_4 > 6 \times 10^9 l./mole$ min., then $nk_3 >$ $5 \times 10^8 l.$ mole⁻¹ min.⁻¹. The lower limit for k_3 is useful in demonstrating a very high specific rate for the Au(II)-Au(III) exchange process, whether by electron or atom transfer.



Fig. 3.—Rate of ferrous-induced exchange. Conditions in text.

The experiments with $Fe(o-phen)_3^{++}$ were performed in the hope of fixing a lower limit of E^0 for Au(II)-AuCl₄⁻, but led to no definite conclusions on this point. Experiment 1.71 shows that Fe^{++} is an effective inducing agent in the presence of $Fe(o-phen)_{3}^{++}$. Evidently the reaction, $Fe(o-phen)_{3}^{++} + Au(II) \rightarrow Fe(o-phen)_{3}^{+++} + Au(II)$, is not rapid compared to exchange between Au(II) and $AuCl_{4}^{-}$. The absence of an induced exchange in experiment 1.72 may be due to slowness in forming Au(II) (unfavorable equilibrium in the first step), or to an inhibitory effect of 1:10 phenanthroline.

The behavior of $Fe(CN)_{6}^{==}$ as an inducing agent is complex. The measurably slow exchange indicated by experiments 1.61 and 1.62 has other causes than a slow reduction of AuCl₄- by Fe- $(CN)_6^{--}$. The net change was studied directly, using the release of Cl⁻ (AuCl₄⁻ + $2e^- \rightarrow AuCl_2^{-}$ $+ 2Cl^{-}$) measured by its radioactivity as index of the extent of reaction. There was an initial rapid release of Cl⁻, half completed in 2 or 3 seconds, and following this, a slow continued liberation proceeding beyond what could be produced by complete oxidation of $Fe(CN)_6^{--}$ to $Fe(CN)_6^{--}$. This shows that $Fe(CN)_6^{--}$ is in part disrupted by $AuCl_4^{--}$, and that CN^{--} also produces Cl^{--} in the system. An independent experiment showed that KCN also releases Cl-. The amount of Clreleased is increased by Fe(CN)⁼, both with $Fe(CN)_6^{=}$ and with CN^- , although $Fe(CN)_6^{=}$ alone causes no release. The results indicate CN transfer during oxidation of $Fe(CN)_6^{--}$, and the reaction seems worthy of further study.

The agents inducing the exchange are not limited to the metal ions mainly dealt with thus far. Tartrate induces a slow exchange, and CN^- , a fairly rapid exchange. Acetaldehyde has no effect.

The agent in distilled water which led to the discovery of the induced exchange processes is believed to be Fe⁺⁺, especially in view of work done partly since the symposium. The rate of disappearance of the agent after mixing with AuCl₄⁻⁻ is similar to that of Fe⁺⁺. The agent is destroyed also by air in basic solution, less effectively by O_2 in neutral solution and very effectively by 0.0004M 1:10 phenanthroline, O_3 and H_2O_2 . Even redistilled water, kept in an ordinary greenish glass container (color presumably due to ferrous), induced some exchange.

A point of general interest in the results is concerned with the mechanism of reduction of AuCl₄– by various reducing agents. The results show without question that the catalytic intermediate Au(II) is present at much lower steady state concentration when the $2e^-$ reducing agents Sb(III) and Sn(II) react, than when Fe⁺⁺ reacts. This comparison suggests the conclusion that the intermediate is not formed by the two-electron reducing agents, or is formed in a much smaller fraction of the acts of reduction for the former substances than for Fe⁺⁺. To meet the objection that Sb(III), although it may generate Au(II), reacts much more rapidly with it than does Fe⁺⁺, an experiment was performed in which the effect of Fe⁺⁺ as inducing agent was tested for a solution also containing Sb(III) (exp. 1.36). This experiment shows that the Au(II) is not appreciably destroyed by Sb(III). The possibility that Sb(IV) and Au(II) are formed by interaction of Au(III) and Sb(III), but that the specific rate of further interaction of these products is much greater than any other changes for them is rendered unlikely if not completely ruled out by noting that the disproportionation of Au(II) proceeds at a rate nearly equal to the collision frequency. An extraordinary selectivity of Au(II) and Sb(IV)exercised in competition with a high disproportionation rate and even in the presence of Fe^{++} , can be understood only if the Au(II) and Sb(IV) are not separated from each other, *i.e.*, if Au(II) is not a true intermediate. The classification of a reaction as a one- or two-electron change is concerned with the question of whether intermediates (or immediate products) characteristic of one or other process are formed, and not with the mechanism of electron transfer in the activated complex. We conclude that the reduction of Au(III) by Sb(III) (and probably by Sn(II)) does in fact bypass Au(II).

A second question of fairly general interest is whether reaction 3 takes place by electron transfer or atom transfer. The former process is indicated if Au(II) participates in the reaction in the form AuCl₄⁼, the latter if as AuCl₃⁻. It is hoped that some evidence about the formula can be obtained from a study of the exchange catalyzed by Au(I). In this system Au(II) may exist in equilibrium with Au(I) and Au(III).

REMARKS

HAROLD L. FRIEDMAN (University of Southern California): Do you know that the active catalyst produced by the inducing agent is not atomic chlorine?

HENRY TAUBE (communicated in part): We cannot rule out this possibility definitely, but we believe it is rather unlikely. In any case, we can make a simple experimental test by looking for exchange induced in the system AuCl₄--Cl⁻ by light acting on molecular chlorine. Our reasons for considering it unlikely are: no exchange is induced by light acting on AuCl₄⁻ (in the system PtCl₆⁻ -Cl⁻, laboratory light produces rapid exchange); in the latter system, the induced exchange is wiped out by Cl₂, proving Cl not to be the intermediate, and leaving Pt(III) as the likely choice, analogous to Au(II) discussed in the present system; Au(II) cannot be powerful enough as an oxidizing agent to generate Cl from Cl⁻. An assignment of values of E^0 consistent with the known over-all value³ of E^0 for Au-AuCl₄⁻, with the instability of Au(I) (probably only slight by analogy to Au(I)) in presence of Br⁻) is

$$\begin{array}{c} -1.10 & -0.95 \\ \text{Au} & \text{AuCl}_2 & \text{AuCl}_4 \\ & \text{Au} & -1.00 \end{array}$$

For Fe⁺⁺ to be efficient in generating Au(II), even in the presence of much Fe⁺⁺⁺, E^0 for Au^{II}_{CI}-AuCl₄-, must be < -0.5, and this means that E^0 for Au^{Cl}₂-Au^{Cl}_{CI} > -1.4, hence Au^{II}_{CI}- cannot generate Cl efficiently from Cl⁻ ($E^0 \sim -2.3$).

Since the symposium it has been found that no exchange is induced in the presence of $10^{-4} M$ Cl₂ and a bright fluorescent light.

(3) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 194.

ANION-EXCHANGE STUDIES. IX.^{1,2} ADSORBABILITY OF A NUMBER OF METALS IN HYDROCHLORIC ACID SOLUTIONS

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The results of anion-exchange studies in hydrochloric acid solutions of the alkali metals, ammonium ions, alkaline earths, elements of Group III, titanium and vanadium, and of palladium, iridium and platinum are given. Negligible adsorption is shown by the alkali metals, ammonium ions, alkaline earths, Al(III), Y(III) and rare earths. Ti(III), V(III), V(IV) and Sc(III) are slightly adsorbed from concentrated HCl, while Ti(IV) and V(V) show considerable adsorption under these conditions. In(III) shows some adsorption between 0.5 and 12 M HCl, and Ga(III) excellent adsorption, with adsorption increasing to 7 M HCl and decreasing beyond this molarity. Tl(III), Pd(II) and Pt(IV) show excellent adsorption between 0.1 and 12 M HCl with adsorption generally decreasing in this range. Ir(III) is negligibly adsorbed in the same range, but adsorbs at very low HCl concentrations. Some implications of these results on separations are illustrated. A striking parallel between anion-exchange adsorption and solvent extraction by ethers is discussed.

In a series of earlier papers from this Laboratory it was demonstrated that anion exchange of metal complexes is a powerful new tool for the separation of ions, as well as for the study of complexing reactions. The investigations at the present time have included a number of the less familiar "elements" which are of interest in this symposium. Some of our results, particularly from the analytical point of view, for the elements titanium and vanadium, scandium and yttrium; gallium, indium and thallium; palladium, iridium and platinum, will be given in this summary. In order to demonstrate the wide applicability of the method, studies are included of a number of elements which were not expected to form negatively charged complexes, namely, the alkali metals, alkaline earths and the remaining elements of Group III.

Experimental

The adsorbability of the elements was studied by both the equilibrium and the column methods.³ In the equilibrium method, measured amounts of resin and solution are agitated, usually for several days, and the resulting decrease in concentration of the metal in the solution used to compute the distribution coefficient D (amount per kg. resin/amount per liter solution).

All distribution coefficients D are calculated with resin

⁽¹⁾ This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

⁽²⁾ Previous paper, K. A. Kraus and F. Nelson, J. Am. Chem. Soc., **75**, 3273 (1953).

^{(3) (}a) K. A. Kraus and G. E. Moore, *ibid.*, **73**, 9 (1951); (b) **75**, 1460 (1953).