691. *The Relative Stabilities of Halogeno-complexes. Part I. The Hexahalogenoplatinates.*

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A radiochemical technique has been used to determine the equilibrium constants for the stepwise interchange of free iodide ions with the halogens in $PtCl_6^{2-}$ or $PtBr_6^{2-}$. At 25°, and at an ionic strength of 0·5M, the values of log β_6 for the chloride : iodide and bromide : iodide systems are $18{\cdot}2_4 \pm 0{\cdot}1$ and $15{\cdot}9_3 \pm 0{\cdot}1$, respectively, the iodide being the strongest complex. Similar measurements were made at 0° and 44·5° and corresponding values of ΔH^0 are -19 ± 1 and -23 ± 1 kcal./g.-ion, and those of ΔS^0 are about 19 and -3 cal./deg. mole. These results are used to calculate the relative standard free energies and enthalpies of formation, and the relative standard entropies, of the hydrated complex ions.

FEW direct measurements have been reported of the relative stability constants of halogeno-complexes, and none of these has been made over a range of temperatures. Such measurements are of interest because the constants can be used to divide metal ions into two classes,[1] (*a*) and (*b*), according to whether the order of affinity of the halide ions is, respectively, F > Cl > Br > I, or the reverse. In the Periodic Table, platinum lies

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[1] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12** 265.

well inside the group of class (*b*) metals, the halogeno-complexes of which decrease in stability from the iodide to the chloride.

The hexahalogenoplatinates are all too stable for measurements of their individual stabilities to be readily made but, with the exception of the fluoroplatinate, they are interconvertible in aqueous solution by addition of sufficient of the appropriate free halide ion. Semiquantitative estimates of the relative stabilities have been made by Schlesinger and Palmateer[2] who used a spectrophotometric method, and Newman and Hume[3] have recently developed this method so that successive equilibrium constants for interchange of halogen ligands can be measured. This depends on the additional determination of several extinction coefficients and we have used an alternative method[4] which proves to be simpler and probably more accurate. It depends on the relative slowness of interchange of the halogen ligands which exemplifies the inertness of nearly all platinum complexes.[5] This enables mixed complex species to be separated from the free anions, by precipitation, without any adjustment of the equilibria taking place such as might occur owing to different solubilities and rates of precipitation of the various species present. Although analysis of the precipitated species for the two halogens present could, in principle, be done by other means, the use of iodine-131 as a tracer makes the analysis very much quicker, without any loss in accuracy. A similar tracer method has been used independently by Dunning and Martin[6] to measure the equilibrium constants for stepwise replacement of chloride in $PtCl_4^{2-}$ by bromide, at 25°.

Procedure.—Varying amounts of labelled iodide solution were added to aliquot parts which consisted of sodium chloro- or bromo-platinate dissolved, respectively, in 1M-sodium chloride or bromide, and the solutions were diluted to an ionic strength, I, of 0·5M. The large excess of free chloride or bromide ions kept the ionic strength constant to within 1%. The solutions were allowed to come to equilibrium at a known temperature and the complex species were then precipitated as their cæsium salts. The activity in the free iodide form was measured, in solution, by using a scintillation counter, and compared with the total iodide activity added. The average number, $\bar{n}$, of iodide ligands in each complex ion, and the ratio of the concentration of free chloride or bromide to that of free iodide, were then calculated and equilibrium curves (corresponding to Bjerrum's formation curves) were plotted. From these curves the six equilibrium constants were derived, by using Bjerrum's method of successive approximations,[7] and enthalpy and entropy changes were determined after repetition of the measurements at two other temperatures. Since the equilibria were studied at a constant ionic strength, and since they involve interchange of very similar ions, the activity coefficients of which will be approximately equal, the concentration constants will be close to the thermodynamic constants and the functions derived from the constants will be within a few units % of the corresponding standard thermodynamic functions. This is supported by a study of the $PtCl_6^{2-}$–I^- system at 25° and $I = 1$M. The equilibrium curve is very close to that obtained at $I = 0{\cdot}5$M and the values of log β_6 which were obtained from the two curves differ by less than 1% ($\beta_6 = K_1K_2 \ldots\ldots K_6$).

By Bjerrum's procedure, temporary constants can be obtained from the equilibrium curves in two ways. In one, the value of $([Cl^- \text{ or } Br^-]/[I^-])_{\text{free}}$ at $\bar{n} = n - \frac{1}{2}$ is taken as an approximate measure of K_n, where n is an integer from 1 to 6. In the other, the average constant, $K_{\text{av.}}$, is taken as the value of $([Cl^- \text{ or } Br^-]/[I^-])_{\text{free}}$ at $\bar{n} = 3$, and values of K_n are obtained from the expression

$$K_n = [(7 - n)/n]\, K_{\text{av.}} x^{7-2n}$$

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[2] Schlesinger and Palmateer, *J. Amer. Chem. Soc.*, 1930, **52**, 4316.
[3] Newman and Hume, *J. Amer. Chem. Soc.*, 1957, **79**, 4571, 4581.
[4] Poë and Vaidya, *Nature*, 1959, **184**, 1139.
[5] Taube, *Chem. Rev.*, 1952, **50**, 69.
[6] Dunning and Martin, *J. Amer. Chem. Soc.*, 1959, **81**, 5566.
[7] Bjerrum, " Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

where x is the " spreading factor " which can be derived [7] from the slope of the equilibrium curve at $\bar{n} = 3$. A correction term, involving either one of the sets of temporary constants, is then applied to the constants given by the former method, and the improved values so obtained can then be used to give a more accurate correction term. Which of the two sets of temporary constants to use initially depends on the value of x, and also on the symmetry of the curves about $\bar{n} = 3$.

The logarithms of the temporary constants for the overall reactions, obtained in these two ways, and of the constants obtained after applying the corrections, are listed in Table 1. The equilibrium curves, derived from constants obtained by the approximation method, show systematic variations from the experimental curves, and the constants after a second cycle of approximations are actually less good than those after only one cycle. The final constants were therefore obtained by a " curve-fitting " procedure which will be described elsewhere, and equilibrium curves, derived from the constants for the $PtCl_6^{2-}$–I^- system, are shown in Fig. 1 together with the experimental points. The values of log β_6 obtained by this procedure are also given in Table 1, the uncertainty being about $\pm 0{\cdot}1$. Values of the individual constants are not given here since only the overall constants are required when considering the relative stabilities of the binary complexes. Similar values of log β_6 are obtained from the different sets of constants and ΔH^0 is not very dependent on which set of values is used. The temperature variations of the " curve-fitting " values are plotted in Fig. 2.

TABLE 1. *Values of log* β_6 *for the systems* $PtCl_6^{2-}$–I^- *and* $PtBr_6^{2-}$–I^-. ($I = 0{\cdot}5$M.)

	Temporary constants from mid-point slope		Temporary constants from $([Cl^- \text{ or } Br^-]/[I^-])_{\text{free}}$ at $\bar{n} = n - \frac{1}{2}$	
Temp.	$PtCl_6^{2-}$–I^- ($x = 0{\cdot}89$)	$PtBr_6^{2-}$–I^- ($x = 1{\cdot}08$)	$PtCl_6^{2-}$–I^-	$PtBr_6^{2-}$–I^-
0°	$19{\cdot}0_2$	$17{\cdot}5_5$	$19{\cdot}3_2$	$17{\cdot}7_4$
25	$18{\cdot}0_8$	$16{\cdot}0_5$	$18{\cdot}2_4$	$16{\cdot}1_9$
44·5	$16{\cdot}9_5$	$15{\cdot}0_8$	$17{\cdot}2_8$	$15{\cdot}3_0$
	Constants after one cycle of corrections		Constants from curve-fitting procedure	
0°	$19{\cdot}4_5$	$17{\cdot}7_5$	$19{\cdot}3_0$	$17{\cdot}7_9$
25	$18{\cdot}2_5$	$16{\cdot}2_0$	$18{\cdot}2_4$	$15{\cdot}9_3$
44·5	$17{\cdot}3_2$	$15{\cdot}3_2$	$17{\cdot}0_9$	$15{\cdot}1_0$

TABLE 2. *Thermodynamic functions at* 25° *and* I = 0·5M.

	$-\Delta G^\circ$ (kcal./g.-ion)	$-\Delta H^\circ$ (kcal./g.-ion)	ΔS° (cal./deg. mole)
$[PtCl_6]^{2-} + 6I^- \longrightarrow [PtI_6]^{2-} + 6Cl^-$ ...	$24{\cdot}6 \pm 0{\cdot}2$	19 ± 1	19 ± 4
$[PtBr_6]^{2-} + 6I^- \longrightarrow [PtI_6]^{2-} + 6Br^-$ ...	$22{\cdot}0 \pm 0{\cdot}2$	23 ± 1	-3 ± 4
$[PtCl_6]^{2-} + 6Br^- \longrightarrow [PtBr_6]^{2-} + 6Cl^-$ ...	$2{\cdot}6 \pm 0{\cdot}4$	-4 ± 2	22 ± 8

The values of ΔG^0, ΔH^0, and ΔS^0, for the complete interchange of halogen ligands, are given in Table 2, the values for the chloride–bromide system having been obtained by difference. The average free energy change per ligand for the chloride–bromide system is about half that for the corresponding platinum(II) system,[6] and rather less than half that for the *trans*-$[Pt(en)_2Cl_2]^{2+}$–Br^- system which has been studied spectrophotometrically.[8] The enthalpy change in the chloro- to bromo-platinate reaction is slightly unfavourable and it is only the increase in entropy of the system which favours the change. Thus Pt(IV) is clearly a class (*b*) species when judged by the relative stability constants of its halogeno-complexes. Ahrland, Chatt, and Davies [1] have emphasised, however, that, in cases where the free energies and enthalpies of formation are in opposed orders (*e.g.*, Me_3N,BMe_3 and Me_3P,BMe_3), the classification must be based on the enthalpies. On this basis the relative stabilities of the halogeno-platinates are $PtCl_6^{2-} > PtBr_6^{2-} \lll PtI_6^{2-}$

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[8] Poë, unpublished work.

and the classification is therefore not so clear. However, the very high relative stability of the iodide supports a predominantly class (*b*) classification.

The relative standard free energies and enthalpies of formation, from the elements in their standard states, of the aqueous complex ions, and the relative standard entropies, can be calculated by using the data in Table 2, together with corresponding values for the aqueous halide ions quoted by Latimer.[9] They are given in Table 3, together with other available data.[9]

FIG. 1. *Equilibrium curves for the chloro- and iodo-platinate system at* (a) 0°, (b) 25°, *and* (c) 44·5°.

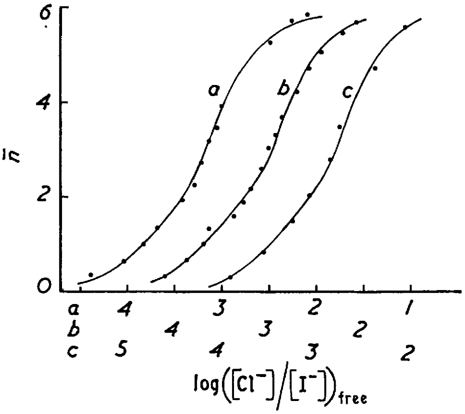

FIG. 2. *Temperature variation of* log β_6: (a) *chloro- and iodo-platinate system,* (b) *bromo- and iodo-platinate system.* (Values of log β_6 obtained by the " curve-fitting " procedure.)

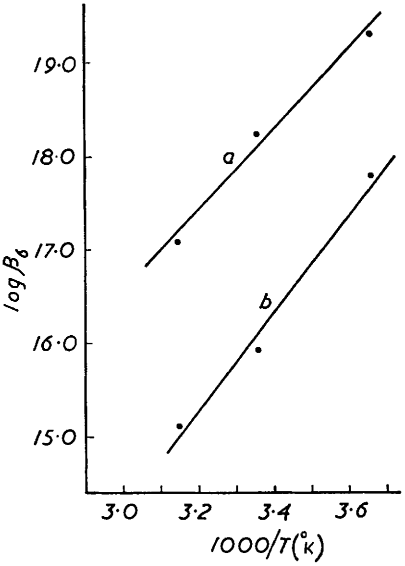

TABLE 3. *Thermodynamic functions for the aqueous hexahalogeno-platinates at* 25°.

	$-\Delta G_f$ (kcal./g.-ion)		$-\Delta H_f$ (kcal./g.-ion)		$\bar{S}^0$ (cal./deg. mole)	
	This work	Latimer[9]	This work	Latimer[9]	This work	Latimer[9]
$[PtCl_6]^{2-}$ ...	x	123·1	y	167·4	z	52·6
$[PtBr_6]^{2-}$	$x - 38$	—	$y - 70$	167·4—50·3	$z + 60$	—
$[PtI_6]^{2-}$ ...	$x - 89$	—	$y - 141$	167·4—111·7	$z + 97$	—

EXPERIMENTAL

Tracer.—Carrier-free iodide-131 was obtained from the Radiochemical Centre, Amersham, in 0·01N-sodium thiosulphate solution. Since thiosulphate can replace iodide from iodoplatinate its concentration was kept negligibly small, either by using as small amounts of the tracer solution as possible, or by treating it with an excess of iodine and removing the unchanged iodine with carbon tetrachloride. The activity in solution was measured by using an Isotope Development Ltd. scintillation spectrometer, adjusted to count the 364 kev γ-rays emitted by the isotope; 5-ml. aliquot parts of the solutions were contained in annular plastic cups which fitted closely round the aluminium cap containing the sodium iodide phosphor.

Reagents.—Platinum complexes were obtained from Messrs. Johnson, Matthey and Co. Ltd. and were used as supplied. Otherwise " AnalaR " reagents were used.

Procedure.—The platinum complex was dissolved in a 1M-solution of the corresponding sodium halide. Aliquot parts of this solution were then diluted with varying amounts of 0·01M-potassium iodide solution containing the tracer, and the final concentration was adjusted

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[9] Latimer, " Oxidation Potentials," Prentice-Hall Inc., New York, 1952.

TABLE 4. *The chloro- and iodo-platinate system.* [Complex] = 0·834 mM. $[Cl^-]_{total}$ = 0·505M.

Temp. (° c.)	Soln. no.	Total activity (counts/min.)	Total $[I^-]$ (10^{-4}M)	Free I^- activity (counts/min.)	Free $[I^-]$ at equil. (10^{-4}M)	n	log $([Cl^-]/[I^-])_{free}$
0	1	3402	3·035	231	0·2060	0·339	4·387
	2	4789	6·070	370	0·4690	0·672	4·028
	3	10,755	9·106	876	0·7420	1·00	3·829
	4	9778	12·14	843	1·047	1·33	3·680
	5	14,370	18·21	1539	1·950	1·94	3·410
	6	23,860	21·25	2887	2·569	2·24	3·289
	7	12,740	25·80	1526	3·089	2·72	3·211
	8	4835	30·35	596	3·741	3·19	3·129
	9	3990	33·38	534	4·486	3·47	3·052
	10	8308	37·94	1096	5·007	3·95	3·002
	11	13,290	60·70	3648	16·65	5·28	2·481
	12	17,990	75·90	6660	28·09	5·73	2·255
	13	19,938	91·06	9227	42·13	5·87	2·079
25	1*a*	531	3·035	73	0·4172	0·314	4·079
	1*b*	1522	3·035	186	0·3709	0·320	4·130
	1*c*	1522	3·035	210	0·4187	0·314	4·077
	1*d*	1522	3·035	201	0·4007	0·316	4·096
	2*a*	1610	6·070	172	0·6485	0·650	3·888
	2*b*	3044	6·070	357	0·7119	0·643	3·847
	2*c*	3044	6·070	341	0·6800	0·648	3·867
	2*d*	3044	6·070	335	0·6679	0·648	3·875
	3*a*	1337	9·105	148	1·008	0·972	3·697
	3*b*	4281	9·105	408	0·8678	0·990	3·761
	3*c*	4281	9·105	460	0·9783	0·975	3·709
	3*d*	4281	9·105	471	1·002	0·971	3·699
	4	4173	12·14	400	1·163	1·32	3·634
	5	2228	15·18	310	2·111	1·57	3·376
	6	2674	18·21	400	2·724	1·86	3·265
	7	3120	21·25	480	3·267	2·16	3·186
	8	12,740	25·80	2081	4·217	2·59	3·076
	9	3632	30·35	600	5·014	3·04	3·000
	10	3990	33·38	701	5·862	3·30	2·932
	11	2608	37·94	480	6·982	3·71	2·858
	12	10,788	45·53	2422	10·22	4·24	2·693
	13	12,590	53·13	3245	13·70	4·73	2·566
	14*a*	4173	60·70	1270	18·48	5·06	2·436
	14*b*	1972	60·70	595	18·31	5·08	2·440
	14*c*	1972	60·70	611	18·80	5·02	2·428
	14*d*	1972	60·70	602	18·53	5·06	2·434
	15*a*	2657	75·90	1055	30·14	5·49	2·224
	15*b*	2465	75·90	991	30·52	5·44	2·218
	15*c*	2465	75·90	982	30·24	5·48	2·222
	16*a*	2674	91·06	1275	43·41	5·71	2·065
	16*b*	2958	91·06	1382	42·54	5·82	2·074
	16*c*	2958	91·06	1410	43·40	5·71	2·066
	16*d*	2958	91·06	1414	43·52	5·70	2·064
44·5	1	598	3·035	122	0·6191	0·289	3·907
	2	1795	9·106	275	1·394	0·925	3·555
	3	2992	15·18	552	2·799	1·48	3·253
	4	4188	21·25	850	4·310	2·03	3·066
	5	1197	30·35	279	7·078	2·79	2·851
	6	1496	37·94	351	8·898	3·48	2·752
	7	2393	60·70	838	21·25	4·72	2·375
	8	3590	91·06	1753	44·46	5·59	2·055

by addition of water. The tubes were stoppered and left in a thermostat to come to equilibrium. The time necessary for equilibrium to be attained was determined by kinetic studies on mixtures corresponding to final $\bar{n}$ values of about 0·7, 2—3, and 4—5. At 25°, about 15 hr. were needed for the chloride–iodide system, and about 30 min. for the bromide–iodide system. When the systems were at equilibrium the complex ions were precipitated as their cæsium salts and, after separation by centrifugation, the supernatant solutions and the washings were diluted to 10 ml. and the activity in 5 ml. was measured to a statistical accuracy of better than ±1%. The total activity present was measured under similar conditions. These measurements, combined with a knowledge of the total concentrations of the species present, permitted

TABLE 5. *The bromo- and iodo-platinate system.* [Complex] = 0·837 mM. $[\mathrm{Br}^-]_{\mathrm{total}}$ = 0·505M.

Temp. (° c.)	Soln. no.	Total activity (counts/min.)	Total $[\mathrm{I}^-]$ (10^{-4}M)	Free I^- activity (counts/min.)	Free $[\mathrm{I}^-]$ at equil. (10^{-4}M)	$\bar{n}$	log $([\mathrm{Br}^-]/[\mathrm{I}^-])_{\mathrm{free}}$
0	1	1582	3·035	160	0·3068	0·326	4·212
	2	2044	6·070	185	0·5495	0·660	3·959
	3	4745	9·106	440	0·8443	0·986	3·773
	4	4088	12·14	401	1·191	1·31	3·624
	5	7908	15·18	845	1·692	1·62	3·490
	6	6132	18·21	766	2·275	1·90	3·343
	7	11,072	21·24	1529	2·935	2·19	3·233
	8	2044	30·35	382	5·672	2·95	2·947
	9	3,955	37·94	900	8·634	3·50	2·765
	10	3066	45·53	810	12·03	4·00	2·622
	11	6327	60·71	2159	20·71	4·78	2·386
	12	5110	75·90	2265	33·64	5·05	2·176
	13	9490	91·06	4809	46·13	5·37	2·039
	14	7154	106·3	4000	59·44	5·59	1·929
	15	12,653	121·4	7622	73·16	5·76	1·839
25	1*a*	683	3·03	92	0·4082	0·313	4·088
	1*b*	1026	3·03	143	0·4244	0·312	4·068
	2*a*	1367	6·06	193	0·8559	0·622	3·767
	2*b*	2053	6·06	281	0·8294	0·625	3·781
	3*a*	2050	9·09	322	1·428	0·915	3·545
	3*b*	3079	9·09	468	1·381	0·923	3·559
	4	4105	12·12	742	2·191	1·19	3·359
	5	5131	15·15	984	2·905	1·46	3·237
	6	6158	18·18	1329	3·922	1·70	3·107
	7*a*	7184	21·21	1756	5·184	1·91	2·986
	7*b*	4783	21·21	1206	5·346	1·90	2·973
	8	1920	30·3	515	8·127	2·65	2·791
	9	2400	37·87	756	11·93	3·10	2·625
	10	2880	45·45	1052	16·61	3·45	2·481
	11	3840	60·6	1701	26·85	4·03	2·273
	12	4800	75·77	2462	38·87	4·41	2·112
	13	5760	90·9	3320	52·37	4·61	1·983
	14*a*	4706	106	2810	63·30	5·11	1·901
	14*b*	4081	106	2450	63·63	5·06	1·899
	15	4664	121·3	3002	78·05	5·17	1·810
	16	6051	136·3	4056	91·35	5·37	1·742
	17	6723	151·5	4703	105·9	5·45	1·678
44·5	1	598	3·035	117	0·5937	0·292	3·926
	2	1165	9·106	240	1·875	0·865	3·427
	3	1553	12·14	335	2·619	1·14	3·282
	4	1942	15·18	476	3·718	1·37	3·130
	5	2330	18·21	590	4·612	1·63	3·036
	6	777	30·35	251	9·804	2·46	2·709
	7	971	37·94	355	1·387	2·88	2·559
	8	1165	45·53	461	1·801	3·29	2·446
	9	1553	60·70	761	29·75	3·70	2·228
	10	1942	75·90	1039	40·59	4·22	2·094
	11	2330	91·06	1359	53·10	4·55	1·977

calculation of both $\bar{n}$ and the concentration ratio of the free halide ions. The results are given in full in Tables 4 and 5. Repetition of some of the measurements showed that the values of $\bar{n}$ obtained from independent experiments were reproducible to within about 2%.

The importance, to the success of this method, of the relative inertness of the equilibria was illustrated by the initial results on the bromide–iodide system at 44·5°. The precipitation of the cæsium salts was noticeably slower than on other occasions and the amount of iodide in the complex was found to be larger than expected, the equilibrium curve overlapping that obtained at 25°. This was understandable if the equilibria were undergoing partial adjustment during the slow precipitation of the complex ions, and if the cæsium salts were less soluble the more iodide that there was present in the complex ion. The use of a much larger excess of cæsium salt ensured a rapid precipitation, so that distortion of the equilibria was minimised.

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