232. *Stabilities of Complex Compounds of Metals. The System Di(tri-*n*-butylphosphine)dichloropalladium*(II)–n-*Octylamine.*

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The successive equilibrium constants for the replacement of *n*-octylamine in $[PdCl_2(C_8H_{17}\cdot NH_2)_2]$ by tri-*n*-butylphosphine have been obtained at 25° in 2 : 2 : 4-trimethylpentane as solvent. This system is characteristic of those useful for studying the equilibria of complexes of metals which do not form simple hydrated ions or of ligands or complexes which are not water-soluble. The absorption spectra of the solutions are used to obtain the concentrations of all three metal-containing compounds in the equilibrium solutions. Since two of the compounds absorb light only in wavelength regions where all three compounds have appreciable extinction coefficients, two new graphical methods for obtaining concentrations from optical-density measurements on mixtures have been developed. The accuracy of each method is shown by application to one set of data, and the results are compared with those obtained by the standard method of solving simultaneous equations.

EQUILIBRIA between complexes of metals which do not form simple hydrated metal ions or of ligands which are insoluble in water or give insoluble complexes, can seldom be studied by conventional methods (see, however, Leden and Chatt [1]). An unreactive organic solvent can be used if a reference ligand other than water is chosen, but it is then necessary to avoid the difficulties caused by ionic association in such liquids. This is most easily done by studying uncharged complexes. The choice of a suitable reference ligand is controlled by several factors: (*a*) The ligand should be monodentate in all circumstances. (*b*) It should co-ordinate to as many different metals as possible. (*c*) To facilitate comparisons between different metals the ligand should form bonds to the metal which are similar for all metals, *i.e.*, "double bonding" and conjugation should be avoided. (*d*) The complexes should be stable and soluble in a wide variety of solvents. (*e*) The free ligand should be readily obtainable, easily purified, and stable.

Nitrogen was considered to be a suitable co-ordinating atom, and a primary aliphatic amine the best class of compound. Availability and consideration of solubility led to the choice of *n*-octylamine. The extensive data existing for the complexes of ammonia in aqueous solution will permit correlation of results in water and other solvents since *n*-octylamine behaves qualitatively in the same way as ammonia, and quantitative studies are possible.

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[1] Leden and Chatt, *J.*, 1955, 2936.

Investigations into the nature of the metal–ligand bond have led to increased interest in the complexes formed by atoms of low electronegativity (P, As, Sb, S, Se, Te, etc.), particularly with Group VIII metals. Such complexes can be studied quantitatively in aqueous solution only in special cases. In this paper, a method is described for studying a system which will permit comparison of the strengths of the bonds from the metal to such atoms. Palladium was selected as a suitable metal since it does not give geometrical isomers under the conditions employed, and tri-*n*-butylphosphine as the phosphorus-containing ligand. The acid radical present was chloride and the solvent found to be most suitable was *iso*octane (2 : 2 : 4-trimethylpentane). The system studied can be represented as follows :

$$[PdCl_2(C_8H_{17}{\cdot}NH_2)_2] + PBu_3 \rightleftharpoons [PdCl_2(C_8H_{17}{\cdot}NH_2)(PBu_3)] + C_8H_{17}{\cdot}NH_2$$
$$[PdCl_2(C_8H_{17}{\cdot}NH_2)(PBu_3)] + PBu_3 \rightleftharpoons [PdCl_2(PBu_3)_2] + C_8H_{17}{\cdot}NH_2$$

The equilibrium constants K_1 and K_2, defined as usual, can be used to give the free-energy change on replacement of *n*-octylamine by tri-*n*-butylphosphine. It has been shown [2] that the di-(*n*-octylamine)- and di(tri-*n*-butylphosphine)-palladous chloride complexes are stable in hydrocarbon solvents and that ionisation equilibria are unimportant. In benzene solution the electrical conductance of either of these compounds is unaffected by the presence of excess of ligand, showing that ionic complexes are not formed. The same is true for (*n*-octylamine)(tri-*n*-butylphosphine)dichloropalladium(II) which has also been prepared. Dissociation and chloride-replacement are not important factors influencing the measured constants therefore, but Chatt [3] has pointed out that complexes of Pt(II) containing both an amine and phosphine give evidence of association in carbon tetrachloride solution.[4]

Dr. L. A. Duncanson kindly studied the infrared absorption spectrum of (*n*-octylamine)(tri-*n*-butylphosphine)dichloropalladium(II) in *iso*octane and found two bands due to non-bonded amino-groups at 3355 and 3318 cm.$^{-1}$ and two broad bands due to hydrogen-bonded amino-groups at 3233 and 3149 cm.$^{-1}$. Because of the absorption due to the solvent it was not possible to determine the association constant, but it is of the order of 10. If the total concentration of the complex is 10^{-5}M, as in the solutions studied here, only about 0·02% will be in the dimeric form, but it is apparent that at higher concentrations any effects due to association will be more significant.

Method.—It is necessary to measure the concentrations of as many as possible of the compounds in the equilibrium mixture and a spectrophotometric method appears to be satisfactory. This permits great freedom in the choice of solvent and is of wide applicability since most metal-complex compounds absorb appreciably in the visible or ultraviolet region of the spectrum. Moreover, the optical density of a mixture of compounds is an additive property. Two methods may be used to obtain equilibrium constants from spectrophotometric data : (*a*) if the extinction coefficients of all the compounds present are known then the mixture can be analysed from its absorption spectrum ; (*b*) if the extinction coefficients of only some of the compounds are known then the change of spectrum on change of concentration of one of the ligands can, under suitable conditions, be used to obtain a formation curve (see also method 4 below).

In the system under consideration all the compounds can be isolated, and their extinction coefficients in *iso*octane measured. The Beer–Lambert law was shown to hold for all the metal complexes present in the equilibrium mixture and for mixtures of them. The optical density D at a particular wavelength of a solution containing the five constituents of the equilibrium mixture is, therefore, given by

$$D = l\,(\varepsilon_1 c_1 + \varepsilon_2 c_2 + \varepsilon_3 c_3 + \varepsilon_n c_n + \varepsilon_p c_p)$$

where l is the length of the light path in the solution and c_1, c_2, c_3, c_n, and c_p are respectively the concentrations (moles/l.) of $[PdCl_2(PBu_3)_2]$, $[PdCl_2(PBu_3)(C_8H_{17}{\cdot}NH_2)]$, $[PdCl_2(C_8H_{17}{\cdot}NH_2)_2]$, $C_8H_{17}{\cdot}NH_2$, and PBu_3 ; ε_1, ε_2, ε_3, ε_n, and ε_p are the molar extinction

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[2] Burkin, *J.*, 1954, 71.

[3] Chatt, personal communication.

[4] Chatt, Duncanson, and Venanzi, *Atti R. Accad. Lincei*, 1954, **17**, 120.

coefficients of the respective compounds at that wavelength. In addition, let M moles/l. be the initial concentration of palladium complex used. Since ε_p is small at all wavelengths used, and it was found that c_p was also small, this equation can be simplified to

$$D = l\,(\varepsilon_1 c_1 + \varepsilon_2 c_2 + \varepsilon_3 c_3 + \varepsilon_n c_n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The extinction coefficients of the compounds at different wavelengths are shown in Fig. 1; ε_n is too small to be shown on this scale. The data are given in Table 1.

Calculation of Concentrations.—The standard, and apparently the simplest, method of obtaining the concentrations of the compounds from the optical densities of the equilibrium solutions is given as method 1. Since the results were not considered to be sufficiently accurate, other graphical methods were used to smooth-out the experimental errors.

Method 1. The four extinction coefficients are measured at four suitable wavelengths, and the optical densities of the equilibrium solution at those wavelengths are measured, giving four simultaneous equations from which the four concentrations can be calculated.

Method 2. Between 3600 and 2900 Å, ε_2, ε_3, and ε_n are almost constant, while ε_1 is larger and changes rapidly with wavelength. Then equation (1) can be written

$$D = l(\varepsilon_1 c_1 + f)$$

where $f = \varepsilon_2 c_2 + \varepsilon_3 c_3 + \varepsilon_n c_n$ and is assumed to be constant between these wavelengths. Hence, a plot of D against ε_1 at a series of wavelengths will give a straight line of slope lc_1. For wavelengths shorter than 3000 Å the points diverge from the line, and determination of c_2 and c_3 depends on a quantitative study of the nonlinearity of this portion of the plot. It is obvious, therefore, that since the component of D due to $\varepsilon_1 c_1$ is considerable, even at these shorter wavelengths, the determination of c_2 and c_3 is very sensitive to experimental errors.

The value of c_1 obtained can be used to permit the calculation of c_2 and c_3 by a similar method. Since the amine is present in large excess, c_n may be taken as the concentration of free amine added in making up the solution, so that equation (1) may be rewritten as

$$D - l\varepsilon_1 c_1 - l\varepsilon_n c_n = l(\varepsilon_2 c_2 + \varepsilon_3 c_3) = \phi$$

where ϕ is known. ε_2 is largest compared with ε_1 between 2500 and 3000 Å, and ϕ is calculated for a number of wavelengths in this range. From the above equation

$$\phi/\varepsilon_3 = l(\varepsilon_2 c_2/\varepsilon_3 + c_3)$$

and a plot of ϕ/ε_3 against $\varepsilon_2/\varepsilon_3$ will give a straight line of slope lc_2 and intercept lc_3. Similarly a plot of ϕ/ε_2 against $\varepsilon_3/\varepsilon_2$ gives a line of slope lc_3 and intercept lc_2.

Method 3. In the previous method, ratios of the extinction coefficients are used to obtain concentrations. Under some conditions it may be preferable to use differences as follows. If c_1 has been determined by method 2 and M is known, then

$$M - c_1 = c_2 + c_3 = x$$

and $$c_3 = x - c_2$$

Substitution for c_3 in $$\phi = l\,(\varepsilon_2 c_2 + \varepsilon_3 c_3)$$

gives $$\phi = l\,(\varepsilon_2 c_2 + \varepsilon_3\{x - c_2\})$$

so that $$\phi = l\,(c_2\{\varepsilon_2 - \varepsilon_3\} + \varepsilon_3 x)$$

or, since $\varepsilon_3 x$ is known at a particular wavelength,

$$\phi - l\varepsilon_3 x = \alpha = lc_2\,(\varepsilon_2 - \varepsilon_3)$$

Hence a plot of α against $(\varepsilon_2 - \varepsilon_3)$ over a suitable wavelength region (2500—3000 Å in this case) will give a straight line of slope lc_2 passing through the origin.

TABLE 1.

λ (Å)	D *	ε_1	ε_2	ε_3	ε_n	$\varepsilon_1 c_1$	$10^3 \varepsilon_n c_n$	ϕ	$10^4\phi/\varepsilon_3$	$\varepsilon_2/\varepsilon_3$	$10^5\phi/\varepsilon_2$	$10^2\varepsilon_3/\varepsilon_2$	α	$10^3\beta$	$(\varepsilon_2 - \varepsilon_3)$
3600	0·304	1663	710	112·3	—	—	—	—	—	—	—	—	—	—	—
3550	0·350	1963	—	109·0	—	—	—	—	—	—	—	—	—	—	—
3500	0·437	2436	747	110·1	—	—	—	—	—	—	—	—	—	—	—
3450	0·596	3355	727	113·0	—	—	—	—	—	—	—	—	—	—	—
3400	0·875	4944	757	116·9	0·0072	—	—	—	—	—	—	—	—	—	—
3350	1·298	7460	752	118·1	—	—	—	—	—	—	—	—	—	—	—
3300	1·864	10,840	776	116·1	—	—	—	—	—	—	—	—	—	—	—
3280	2·140	12,160	—	—	—	—	—	—	—	—	—	—	—	—	—
3250	2·504	14,380	792	107·5	—	—	—	—	—	—	—	—	—	—	—
3230	2·718	15,720	—	—	—	—	—	—	—	—	—	—	—	—	—
3200	2·960	17,070	820	97·5	0·0126	—	—	—	—	—	—	—	—	—	—
3170	3·048	17,650	843	88·7	0·0216	—	—	—	—	—	—	—	—	—	—
3150	3·006	17,430	865	82·1	—	—	—	—	—	—	—	—	—	—	—
3130	2·890	16,710	872	—	—	—	—	—	—	—	—	—	—	—	—
3100	2·590	14,990	901	69·7	—	—	—	—	—	—	—	—	—	—	—
3050	1·881	10,910	943	58·8	—	—	—	—	—	—	—	—	—	—	—
3000	1·183	6711	996	58·2	0·0232	1·150	1	0·032	5·502	17·12	3·21	5·84	0·030	−2	938
2950	0·704	3827	1143	68·6	—	0·656	1	0·047	6·851	16·66	4·11	6·00	0·045	−13	1074
2900	0·467	2423	1500	101·4	0·0443	0·415	2	0·050	4·931	14·79	3·33	6·76	0·047	−6	1399
2850	0·400	1854	2349	166·6	0·0697	0·318	3	0·079	4·742	14·10	3·36	7·09	0·074	−9	2182
2800	0·404	1642	3832	288·1	0·131	0·281	6	0·117	4·061	13·30	3·05	7·52	0·109	−2	3544
2770	0·408	1544	4929	401·1	—	0·265	7	0·136	3·391	12·29	2·76	8·14	0·124	11	4528
2750	0·406	1428	5637	490·7	0·181	0·245	8	0·153	3·118	11·49	2·71	8·71	0·138	15	5146
2730	0·400	1295	6296	593·2	—	0·222	8	0·170	2·866	10·61	2·70	9·42	0·152	18	5703
2720	0·395	1221	6543	664·0	—	0·209	9	0·177	2·666	9·85	2·71	10·15	0·157	18	5879
2710	0·389	1166	6766	721·2	—	0·200	10	0·179	2·482	9·38	2·65	10·66	0·168	23	6045
2700	0·380	1133	6918	792·6	0·229	0·194	10	0·176	2·221	8·73	2·54	11·46	0·152	31	6125
2690	0·372	1064	6987	872·4	—	0·182	10	0·180	2·063	8·01	2·58	12·49	0·154	29	6115
2680	0·364	995	7036	907·3	0·246	0·171	10	0·183	2·017	7·76	2·60	12·89	0·156	27	6129
2670	0·354	948	6987	1031	—	0·162	10	0·182	1·765	6·78	2·61	14·76	0·151	27	5956
2660	0·344	913	6918	1105	0·263	0·156	10	0·178	1·611	6·26	2·57	15·97	0·145	29	5813
2650	0·335	886	6766	1201	—	0·152	11	0·172	1·432	5·63	2·54	17·75	0·136	30	5565
2630	0·319	837	6249	1381	0·287	0·143	12	0·164	1·187	4·52	2·63	22·11	0·123	23	4868
2600	0·308	891	5265	1631	0·311	0·153	13	0·142	0·871	3·23	2·70	30·97	0·093	15	3634
2580	0·316	1010	4566	1788	0·336	0·173	14	0·129	0·721	2·55	2·83	39·2	0·076	7	2778
2560	0·344	1226	3897	1940	0·368	0·210	16	0·118	0·605	2·01	3·03	49·8	0·060	−1	1957
2540	0·395	1581	3286	2062	0·415	0·271	18	0·106	0·514	1·59	3·23	62·7	0·044	−8	1224
2520	0·474	2050	2910	2181	0·494	0·351	21	0·102	0·468	1·33	3·51	75·0	0·037	−15	729
2500	0·590	2684	2727	2335	0·631	0·460	27	0·103	0·441	1·17	3·78	85·6	0·033	−22	392

* Optical densities refer to a 1·0 cm. cell.

Similar substitution for c_2 and subsequent rearrangement (since $\varepsilon_2 > \varepsilon_3$ throughout the wavelength region used) gives

$$l\varepsilon_2 x - \phi = \beta = lc_3\,(\varepsilon_2 - \varepsilon_3)$$

Method 4. This method for obtaining the equilibrium constants may be used when it is possible to measure the concentration of only one of the complexes present in the equilibrium mixture. It requires data for a number of different equilibrium solutions with a range of concentrations of the determinable constituent. For this reason it was not used in the present investigation, the simpler methods being adequate.

Since di-(*n*-octylamine)dichloropalladium(II) has no appreciable absorption peak except at wavelengths shorter than 2500 Å, where all palladium complexes of this type absorb, this compound will not be the one which is determined. It is convenient, therefore, to re-write the equilibria and put $p_2 = 1/K_1$ and $p_1 = 1/K_2$. It is apparent that for a solution containing a given quantity of bis-phosphine complex and free amine mixed together there will exist a relation between these concentrations, the amount of phosphine complex converted into the other two complexes, and the two equilibrium constants. It is assumed that the bis-phosphine complex is the constituent which can be determined, so that M and c_1 are known, and hence the amount of the compound converted into the phosphine-amine and bis-amine complexes (x). Then

$$p_1 = (x - c_3)(c_p)/c_1c_n$$

and since

$$c_p = c_2 + 2c_3 = x + c_3$$

$$p_1c_1c_n = (x - c_3)(x + c_3)$$

and

$$c_3^2 = x^2 - p_1c_1c_n$$

Similar manipulation of the equation for p_2 gives

$$p_2c_nx - c_3(p_2c_n + x) - c_3^2 = 0$$

Substitution for c_3 and c_3^2 in terms of p_1 then gives

$$p_2c_nx - (p_2c_n + x)(x^2 - p_1c_1c_n)^{\frac{1}{2}} - (x^2 - p_1c_1c_n) = 0 \quad . \quad . \quad . \quad (2)$$

The following treatment of this equation was suggested by Mr. E. W. Balson. An upper limit is set for p_1 by $p_1 \ngtr x^2/c_1c_n$. Putting $x^2 - p_1c_1c_n = \psi$, we can write (2) as

$$p_2c_nx - (p_2c_n + x)\,\psi^{\frac{1}{2}} - \psi = 0$$

$$\therefore \qquad p_2(c_nx - c_n\,\psi^{\frac{1}{2}}) - x\psi^{\frac{1}{2}} - \psi = 0$$

and

$$p_2 = (x\psi^{\frac{1}{2}} + \psi)/c_n(x - \psi^{\frac{1}{2}})$$

From a series of equilibrium solutions a set of limiting values for p_1 can be found. Setting p_1 equal to a series of arbitrary values less than these limiting values, we can calculate a set of values for p_2. A value of p_1 is found for which the spread in the values of p_2 is least. Alternatively, for a given equilibrium solution several possible values of p_1 can be chosen, the corresponding values of p_2 calculated, and the results plotted with p_1 and p_2 as ordinates. If the curves for a number of solutions are plotted together, the point of intersection will give the true values of p_1 and p_2.

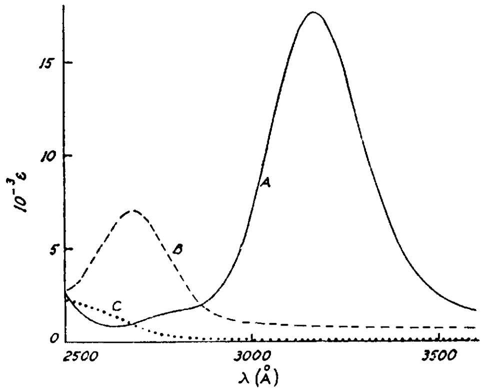
DISCUSSION AND RESULTS

Detailed results are presented (Table 1) for one solution in which the concentrations of the compounds were such that convenient optical densities were obtained over the whole wavelength range by using 5, 10, and 20 mm. cells. In many other cases the solution had to be diluted in order to obtain c_1. In order to show the value and limitations of the different methods described above, the data are treated by each method separately.

Method 1. By using the data for 3170, 2680, and 2500 Å, and correcting D for ε_nc_n, those combinations of the equations considered to be most likely to be reliable gave the results shown in Table 3. The minimum total concentration is $2{\cdot}115 \times 10^{-4}$ which is 105% of M.

Method 2. The excellent straight line obtained by plotting ε_1 against D between 3600 and 3000 Å gives $c_1 = 1{\cdot}713 \times 10^{-4}$. It was found that small amounts of impurities or other systematic errors in the determination of ε_1 caused non-linearity or, frequently, two parallel lines, one for wavelengths below 3170 Å and the other for longer wavelengths. Figs. 2 and 3 show the results plotted to obtain c_2 and c_3. In a consideration of these and Fig. 4, the following facts are significant : (*a*) at wavelengths longer than 2850 Å, ε_1 is rising rapidly while ε_2 and ε_3 are falling slightly or are constant; (*b*) between 2850 and 2700 Å ε_1 changes little; (*c*) ε_2 is a maximum at about 2680 Å.

FIG. 1.



A, ε_1, $[PdCl_2(PBu_3)_2]$
B, ε_2, $[PdCl_2(PBu_3)(C_8H_{17}{\cdot}NH_2)]$
C, ε_3, $[PdCl_2(C_8H_{17}{\cdot}NH_2)_2]$

FIG. 2.

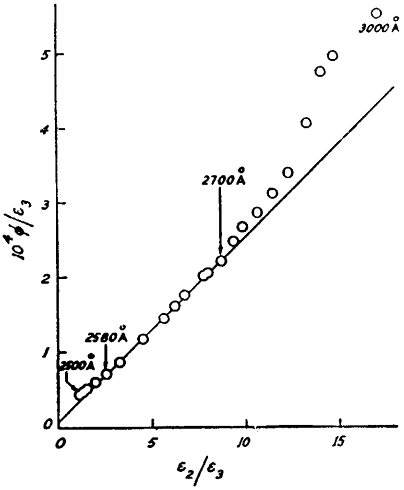
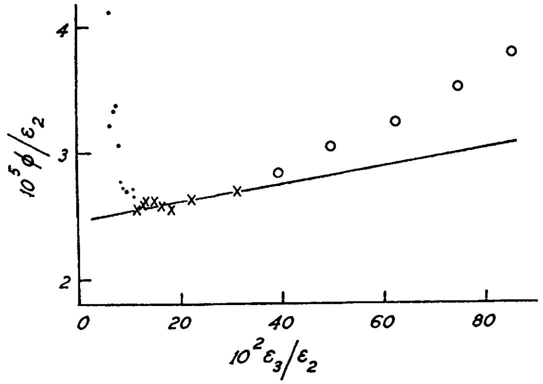
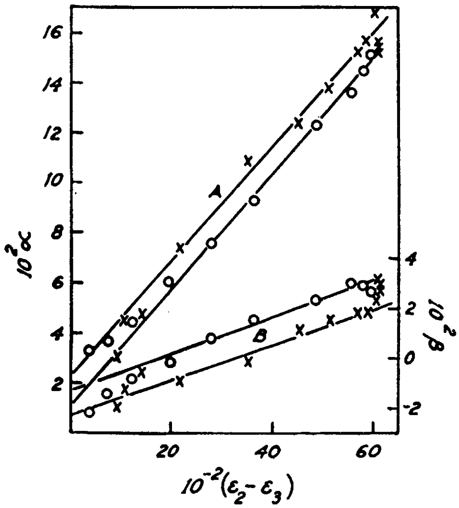


FIG. 3.



Data for wavelengths : ●, 3000—2710; ×, 2700—2600; ○, 2580—2500 Å.

FIG. 4.



Lines A refer to α, B to β. Data for wavelengths : ×, 3000—2680; ○, 2670—2500 Å.

Fig. 2 shows a good straight line between 2700 and 2580 Å, the slope of which gives $c_2 = 2{\cdot}47 \times 10^{-5}$, and the intercept, $c_3 = 0{\cdot}7 \times 10^{-5}$. Putting the intercept equal to $2{\cdot}47 \times 10^{-5}$ in Fig. 3 we can draw the best line for the results between 2700 and 2580 Å, the slope giving $c_3 = 0{\cdot}70 \times 10^{-5}$. The large deviation from the line of the results at wavelengths outside this region is due to normal experimental error magnified by the method of plotting. This is shown by considering separately the three possible sources of error. (*a*) ϕ in error. The value of ϕ which would give linearity over the whole of the wavelength region between 2500 and 3000 Å can be calculated from Figs. 2 and 3. The error ($\Delta\phi$) in ϕ is the same in each case and can be due either to an error in the optical density equal to $\Delta\phi$, or to an error in either $\varepsilon_1 c_1$ or $\varepsilon_n c_n$, best expressed as a percentage error. In Table 2 $\Delta\phi$ has been expressed as a percentage of $\varepsilon_1 c_1$. (*b*) ε_2 in error. From Fig. 2 the value of $\varepsilon_2/\varepsilon_3$ and hence of ε_2 necessary for linearity can be calculated. (*c*) ε_3 in error. The value of ε_3 necessary for linearity can be obtained similarly from Fig. 3.

Examination of Fig. 3 and the calculated corrections expressed as $100\varepsilon_{\text{obs.}}/\varepsilon_{\text{calc.}}$ (Table 2) shows that the source of error is most unlikely to be the value of ε_3. Although an error of less than 10% in ε_2 would give linearity between 2770 and 2710 Å, much greater errors are necessary to correct the data for longer wavelengths. The most probable source of error appears, therefore, to be ϕ. Of the terms comprising this, ε_n is so small that it cannot be the source of error (see Table 2). Although the optical-density measurements were generally reproducible to 0·005, the possible experimental error was considered to be $\pm$0·01 and is likely to be greatest where D is changing rapidly with wavelength since both prism-setting and slit-width are then important factors. This error will not wholly account for $\Delta\phi$, but since a 1% error in either ε_1 or c_1 would eliminate the residue, it is considered that the deviations from linearity shown in Figs. 2 and 3 are due to normal experimental errors in determining the optical density of the equilibrium solution or the solutions used to obtain ε_1.

TABLE 2.

λ (Å)	$\Delta\phi$	D	$10^3\varepsilon_n c_n$	$\varepsilon_1 c_1$	$\frac{100\Delta\phi}{\varepsilon_1 c_1}$	$\frac{100\varepsilon_2\text{(obs.)}}{\varepsilon_2\text{(calc.)}}$	$\frac{100\varepsilon_3\text{(obs.)}}{\varepsilon_3\text{(calc.)}}$
3000	0·007	1·183	1	1·150	0·6	77·8	7·1
2900	0·012	0·467	2	0·412	2·9	75·1	6·8
2800	0·020	0·404	6	0·281	7·1	82·2	12·0
2750	0·010	0·406	8	0·245	4·1	93·8	34·3
2730	0·010	0·400	8	0·222	4·5	94·3	38·9
2720	0·009	0·395	9	0·209	4·3	93·8	41·3
2710	0·006	0·389	10	0·200	3·0	96·2	58·6

Method 3. The value of c_1 was taken as $1{\cdot}713 \times 10^{-4}$, giving $x = 2{\cdot}99 \times 10^{-5}$. Plotting α or β against ($\varepsilon_2 - \varepsilon_3$) gives two parallel lines in each case, the points for wavelengths between 2720 and 2650 Å scattering between the two lines. This region corresponds to the peak of ε_2 and suggests that there is a systematic error in ε_2 on one side of the absorption peak. Such an error could be due, *e.g.*, to slight disproportionation of the phosphine–amine complex, used to determine ε_2. If the value of α at 2850 Å is to lie on the line drawn for wavelengths below 2600 Å (Fig. 4), then ε_2 must be approximately 2800, not 2349, giving ($\varepsilon_2 - \varepsilon_3$) = 2633. The amended value of β is then 0·0047 and the data for 2850 Å fall precisely on the line drawn for wavelengths below 2650 Å. It is apparent, therefore, that the existence of two parallel lines in this method can be explained quantitatively in terms of a systematic error in ε_2 on one side of the absorption peak. Since the lines are parallel, however, the values of c_2 and c_3 obtained are not affected. The lines do not pass through the origin, and this appears to be due largely to errors in α and β, but, again the slopes are not affected. Deviations from the lines occur at wavelengths above 2850 and below 2560 Å for reasons similar to those discussed under method 2. The value of c_2 obtained from Fig. 4 is $2{\cdot}29 \times 10^{-5}$, and Fig. 6 gives $c_3 = 0{\cdot}75 \times 10^{-5}$.

Summary of Results.—The results obtained for the equilibrium solution discussed above are given in Table 3. It is apparent that the value of c_3 obtained by method 1 is valueless, and c_2 depends on the wavelength chosen for the calculations, being fairly reliable. The values of c_2 obtained by methods 2 and 3 differ considerably, and although that from the former is probably the more reliable, the total concentration from the latter is closer to M. Values of K_1 and K_2 are, therefore, calculated from both sets of figures.

Other equilibrium solutions gave results essentially similar to those detailed above.[5] Three separate solutions were studied by the techniques described below, each being diluted sufficiently to give suitable optical densities within the wavelength ranges used to measure

[5] Meddings, Thesis, Southampton Univ., 1955.

TABLE 3.

Method	10^4c_1	10^5c_2	10^5c_3	10^5c_p	$100(c_1 + c_2 + c_3)/M$	$10^{-3}K_1$	$10^{-3}K_2$
1	1·713	2·46	2·02	—	—	—	—
		2·42	1·60		105		
			1·85				
2	1·713	2·47	0·7	—	—	—	—
			0·70	3·87	101	3·93	7·72
3	—	2·29	0·75	3·79	100	3·47	5·50

$M = 2{\cdot}012 \times 10^{-4}$; $c_n = 4{\cdot}306 \times 10^{-2}$.

the three concentrations. Pairs of solutions from the same stock solution are bracketed together, and in each case c_1 was obtained from the more dilute solution. Concentrations used in calculating the equilibrium constants were obtained by method 2, since c_2 and c_3 obtained by method 3 were similar but subject to some uncertainty in choice of the line through the experimental points.

10^4M	2·012	6·946	2·510	2·484	1·374
10^2c_n	4·306	21·01	7·59	2·064	1·142
$\log K_1$	3·59	3·42	3·34	3·45	3·72
$\log K_2$	3·89	4·12	4·34	3·98	—

Hence the equilibrium constants for the system at 25° are

$$\log K_1 = 3{\cdot}34 - 3{\cdot}72;\ -\Delta G_1 = 4{\cdot}56 - 5{\cdot}07 \text{ kcal.}$$

$$\log K_2 = 3{\cdot}89 - 4{\cdot}34;\ -\Delta G_2 = 5{\cdot}30 - 5{\cdot}92 \text{ kcal.}$$

EXPERIMENTAL

The spectrophotometer used was the Hilger " Uvispek." The wavelength drum was checked for accuracy periodically, and the density scale was tested by using pure potassium nitrate solutions of different concentrations in 0·5 and 1·0 cm. cells, at 3010 Å. Plotting the extinction coefficient found for each solution against the optical density should give a straight line parallel to the density axis. It was found that optical density values smaller than 0·4 became increasingly unreliable (usually too high), and that values larger than 1·3 are also unreliable (too low). Accordingly, wherever possible, optical density measurements were confined to the range $D = 0{\cdot}4$—$1{\cdot}3$. The silica absorption cells were cleaned in hot detergent (" Teepol ") solutions, thoroughly rinsed in running hot water and a jet of distilled water, and dried *in vacuo* over phosphoric oxide.

It was found that the tributylphosphine in the equilibrium mixture was decomposed by oxygen or water, so the solutions were prepared and studied in an inert atmosphere. A new cell holder for the spectrophotometer was made, therefore, so that the cells could be kept air-tight and maintained at a constant temperature. A block of high-purity copper was used, drilled so that water pumped from a constant-temperature bath circulated through the walls of the holder, keeping the temperature constant within ±0·1°. The bottom of each cell compartment was covered by a strip of soft thin rubber, and the undersurfaces of the cell lids were ground flat and covered with a cellulose adhesive tape. The mild-steel cover of the cell holder screwed down, and pressure screws on to the individual cell lids could be tightened to make gas-tight seals. Solutions were prepared and the cells filled and sealed in a " manipulation box " containing commercial nitrogen and a residual air concentration of less than 0·1% of the gas present.

Preliminary experiments indicated that, if appreciable concentrations of amine-containing complexes were to be present in the equilibrium mixture, the concentration of tributylphosphine present must be very small and the amount of *n*-octylamine relatively large. These requirements were most easily met by using the bis-phosphine–palladium complex and adding amine. In view of the small quantities of the complex required and the relative complexity of the technique used to make up the reaction solutions, stock solutions of the materials were made up for each set of mixtures studied. To increase the accuracy with which the starting concentrations were known, the quantities of stock solutions and solvent used were weighed. If suitable precautions are taken, this is probably unnecessary now that the validity of the methods used to treat the data is established.

Stock solutions of the phosphine complex were prepared in a stoppered volumetric flask by weighing solid and solvent. Stock solutions of *n*-octylamine were prepared as follows. Pure redistilled amine was again distilled at 16 mm. immediately before use, the condenser passing through a sealed hole into the manipulation box. The requisite volume of amine was added to a weighed quantity of *iso*octane in a weighed Pyrex-glass tube with a constriction a little below the top. A quill tube inside a second tube was used for the introduction to avoid wetting the top or neck of the tube. Into the constriction was put a piece of glass rod which fitted tightly but did not fall through. The tube was suspended by a clamp above the constriction, and a coil of nichrome wire wound around this was connected through a suitable resistance to the A.C. mains. As the glass softened, the weight of the bulb and contents caused the neck to pull out until it was in contact with the rod, which then softened and sealed the bulb. This was later removed from the box and weighed to obtain the weight of amine present.

The tubes in which equilibrium was attained were similar but had a second constriction at the top. After they had been cleaned and dried by repeated evacuation and introduction of dried air, the tubes were evacuated to 10^{-2} mm. and tested to ensure that no pinholes were present, and the top constriction was sealed, a deep scratch being made later. Each tube was put in a wire cradle so that it would stand upright and had a piece of rubber tubing sealed with glass rod fitted over the sealed constriction to act as a stopper later. The tube, stopper, and rod to be used for sealing the lower constriction were weighed together and a number of such sets were introduced into the manipulation box. The top seal was broken off at the scratch and a measured amount of the stock phosphine complex was introduced through a quill and guard tube. The tube was stoppered, removed from the box together with the glass fragment broken off, and weighed. It was put back into the box, amine solution was added in the same way, and the tube removed and weighed. In each case the stoppered tube was in the air for only a few minutes. It was then sealed, or the mixture was divided into several portions by pouring into other tubes in the box, each of these being sealed by electric heating as described above, removed from the box, re-sealed in a flame just below the stopper, and kept at 25°. When necessary, the solutions were further diluted by a similar technique before measurements were made. The absorption cells were filled and clamped in the cell holder in the nitrogen-filled box.

Solutions of the bis-phosphine, phosphine-amine, and bis-amine complexes to be used for measurement of the extinction coefficients were prepared by weighing in the open laboratory. To obtain appreciable optical-density values, the concentration of *n*-octylamine used in the determination of ε_n had to be approximately 100 times the concentration present in an equilibrium mixture.

Since all solutions were prepared by weight while concentrations were required to be expressed in moles/l., it was shown that mixtures of *n*-octylamine and *iso*octane containing up to 38% of amine show a linear relationship between amine concentration and density.

Materials.—*iso*Octane (2 : 2 : 4-trimethylpentane) was obtained from the Esso refinery at Fawley, Hants. It was redistilled before use; d^{25} 0·6877.

n-*Octylamine.* The commercial material from Armour and Co. was fractionated *in vacuo* several times, b. p. data given by Ralston *et al.*[6] being accepted.

Di-(n-*octylamine*)*dichloropalladium*(II). Palladous chloride (2·7 g.) and ammonium chloride (1·63 g., 2 mol.) were dissolved in water (150 c.c.) in a 250 c.c. stoppered bottle, and *n*-octylamine (4·0 g., 2 mol.) added. After 2 hours' shaking, the precipitated *complex* was filtered off, dried, and recrystallised from light petroleum (b. p. 80—100°); it had m. p. 112·5° (Found: C, 44·5; H, 8·6; N, 6·6. $C_{16}H_{38}N_2Cl_2Pd$ requires C, 44·1; H, 8·8; N, 6·4%).

(*Tri-*n-*butylphosphine*)(n-*octylamine*)*dichloropalladium*(II). Di(tri-*n*-butylphosphine)dichloro-μ-dichlorodipalladium(II) (1·906 g.) was dissolved in the minimum amount of warm benzene, and *n*-octylamine (0·643 g., 2·00 mol.) added to the cooled solution. The benzene was removed *in vacuo*, leaving the required *complex* as a viscous, golden-yellow oil. Attempts to crystallise this by cooling it, or its solutions in many solvents, to −40° were unsuccessful, but disproportionation occurred in some solvents, the phosphine complex crystallising (Found: C, 46·6; H, 9·1; N, 3·0. $C_{20}H_{46}NCl_2PPd$ requires C, 47·2; H, 9·1; N, 2·75%). The absorption spectrum proves that the compound is not a mixture of the bis-phosphine and bis-amine complexes and contains no bridged compound.

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[6] Ralston, Selby, Pool, and Potts, *Ind. Eng. Chem.*, 1940, **32**, 1093.