72. *Studies with Dithizone. Part III.* The Extraction Constant of Zinc Dithizonate.*

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The extraction of zinc as its dithizone complex into chloroform and carbon tetrachloride has been investigated for a wide range of reagent concentrations and from aqueous buffers of different pH and ionic strength. The extraction constants under the conditions of zero ionic strength are ~10 and 130 ± 4, respectively. Partition equilibrium has been approached for the first time from both sides, and the general and specific effects of salt present in the aqueous phase have been studied. The new data have been used to test theoretical equations previously deduced for the partition equilibria of metal complexes, and certain modifications are proposed when the activity coefficients of the reacting species must be taken into account or when water-soluble metal complexes participate in the partition equilibria. The composition of zinc dithizonate has been confirmed by spectrophotometric measurements, the method of continuous variations being used.

If a solution of a monobasic organic acid, HR, in a solvent immiscible with water is shaken with an aqueous solution of an n-valent kation, M^{n+}, under such conditions that there results a metal complex, MR_n, soluble in organic solvents though sparingly soluble in water, the situation when partition equilibrium has been attained can be represented by:

$$[MR_n]_o/[M^{n+}]_w = E = K([HR]_o/\{H\}_w)^n \qquad . \quad . \quad . \quad . \quad . \quad (1a)$$

whence

$$\log_{10} E = \log_{10} K + n \log_{10} [HR]_o + n\text{pH} \qquad . \quad . \quad . \quad . \quad (1b)$$

where the subscripts w and o refer to the aqueous and the organic phases, respectively. The assumptions made in deriving this equation have been discussed in a previous paper (Irving and Williams, *J.*, 1949, 1841) where it was shown that the extraction constant $K = (K_r p_r)^n/(K_c p_c)$, where K_r and K_c are the dissociation constants and p_r and p_c the partition coefficients between water and organic solvent of the reagent, HR, and complex, MR_n, respectively.

Experimental verification of equation (1) requires, in addition to measurements of the extractability, E, at various acidities, a knowledge of the term $[HR]_o$, the concentration of reagent in the organic phase *in excess* of that required for complex formation. Now if

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* Part II, *J.*, 1949, 1847.

V_w, V_o are the volumes of aqueous and organic phases and M_{HR} is the total amount of reagent in the whole system (expressed in g.-mol.) we have

$$M_{\mathrm{HR}} = V_w([\mathrm{HR}]_w + [\mathrm{R}']_w + n[\mathrm{MR}_n]_w) + V_o([\mathrm{HR}]_o + n[\mathrm{MR}_n]_o)$$

$$= \big(V_w p_r(1 + K_r/\{\mathrm{H}\}) + V_o\big)[\mathrm{HR}]_o + n(V_w p_c + V_o)[\mathrm{MR}_n]_o \quad . \quad . \quad (2)$$

A knowledge of p_r, K_r, and pH being assumed, the term $[\mathrm{HR}]_o$ can obviously be calculated from the known total amount of reagent taken provided the second term in equation (2) can be neglected in comparison with the first, a condition which can be realised experimentally by using an amount of reagent which is very large in comparison with that of the metal extracted. Indeed, under conditions where $[\mathrm{HR}]_o$ may be regarded as effectively constant, it follows from equation (1*b*) that a plot of $\log_{10} E$ against pH should be a straight line of which the integral slope, n, would confirm the empirical formula of the extractable species. This prediction has been confirmed by Suttle (Atomic Energy Commission Declassified Report 2800) for partition equilibria involving ^{140}La and 1-thenoyltrifluoroacetone (T.T.A.; cf. Irving, *Quart. Reviews*, 1951, V, 223).

If, however, the amount of metal extracted becomes comparable with the available amount of reagent, the problem becomes more complex. This is the case when diphenylthiocarbazone ("dithizone"; HDz) is used in trace-metal determinations, for since both the reagent and its metal complexes are strongly coloured, the sensitivity of absorptiometric determinations by reversion (Irving, Risdon, and Andrew, *J.*, 1949, 537) or by other methods (Sandell, "Colorimetric Determination of Traces of Metals," 2nd edn., New York, 1950) increases as the ratio $nV_o[\mathrm{MR}_n]_o/M_{\mathrm{HR}}$ approaches unity. Whilst on the one hand the high molecular extinction coefficient of dithizone (in carbon tetrachloride, $\varepsilon = 3{\cdot}5 \times 10^4$ at $\lambda_{\mathrm{max.}} = 615$ mμ) facilitates the determination of $[\mathrm{HDz}]_o$ by absorptiometry even in the presence of most of its strongly coloured metal complexes (which absorb comparatively feebly at this wave-length), yet instrumental considerations limit the useful concentration of dithizone to $<10^{-4}$M, a concentration which becomes comparable with the level of trace-metal concentrations involved, *viz.*, 0—10 p.p.m. On the other hand, dithizone fulfils two of the essential conditions postulated in deriving equation (1), for it has recently been shown (*a*) to exist as unassociated molecules in both aqueous and organic phases (Irving, Cooke, Woodger, and Williams, *J.*, 1949, 1847) and (*b*) to behave as a monobasic acid of pK about 4·5 (Irving *et al.*, *loc. cit.*; and unpublished work; Sandell, *J. Amer. Chem. Soc.*, 1950, **72**, 4660). Moreover, if the pH of the aqueous phase is at least 2 units below $\mathrm{pH}_{\frac{1}{2}}$, the hydrogen-ion exponent for 50% extraction (8·9 and 10·6 for carbon tetrachloride and chloroform systems, respectively), less than 1% of the un-complexed dithizone will partitioni nto the aqueous phase so that the absorbancy [*] of the organic extract measured at $\lambda_{\mathrm{max.}}$ for dithizone will be a satisfactory measure of $[\mathrm{HDz}]_o$. This condition $\mathrm{pH} \ll \mathrm{pH}_{\frac{1}{2}}$ can also be expressed in the form $p_r K_r/\{\mathrm{H}\} \ll 1$, and introducing this into equation (2), we have for the case where $V_o = V_w$:

$$[\mathrm{HR}]_{\mathrm{initial}} = M_{\mathrm{HR}}/V_o = [\mathrm{HR}]_o + n[\mathrm{MR}_n]_o \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Provided, therefore, that no other species participate in the extraction equilibria (*q.v.*), measurements of the absorbancies of the organic phases before and after the extraction of zinc dithizonate (and the concomitant disappearance of an equivalent amount of dithizone) will permit of the determination of both $[\mathrm{HR}]_o$ and $[\mathrm{MR}_n]_o$ once a calibration curve has been set up.

The ideal system for quantitative verification of equation (1) demands *inter alia* a metal which forms a single dithizone complex and one which shows the least tendency to

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[*] T_{solution} (the overall rectilinear *transmittance* of an absorption cell with parallel transparent windows of, *e.g.*, glass or fused quartz, containing a solution or homogeneous mixture of solids, liquids, vapours, or gases, of which the compound of interest is the solute or one constituent) is defined as the ratio of the homogeneous radiant energy leaving the back face of the cell to that.incident at right-angles upon the front face. T_{solvent} is the (overall) transmittance of the same, or a duplicate, cell containing pure solvent or the same mixture in the same relative proportions minus the constituent of interest. The *transmittancy* of the sample is given by $T_s = T_{\mathrm{solution}}/T_{\mathrm{solvent}}$, and the *absorbancy* of the sample is defined by $A_s = -\log_{10} T_s = \log_{10} (T_{\mathrm{solvent}}/T_{\mathrm{solution}})$. (Cf. *Nat. Bur. Standards*, Letter Circular 1947, LC-857; Mellon, *Analyt. Chem.*, 1949, **21**, 3.)

complex with any possible component of the buffers employed. Accurate measurement of the pH of the aqueous phase contra-indicates the use of very strongly acid or very strongly alkaline media and calls for a metal complex of neither too large nor too small stability (cf. Irving and Williams, *Nature*, 1948, **162**, 746). Despite its amphoteric character (*i.e.*, its tendency to form competitive complexes with hydroxyl ions at high alkalinities) the bivalent metal zinc most completely fulfils these conditions, and equilibrium in the zinc–dithizone system should be representable by equation (1) with HR = HDz, M = Zn, and $n = 2$.

Preliminary measurements by Kolthoff and Sandell (*J. Amer. Chem. Soc.*, 1941, **63**, 1906) summarised in Table 1 show that substantially constant values are obtained for *K* even when the extractability is varied 100-fold and the excess of dithizone from 25% to 2000%. It has, however, been pointed out [Irving and Williams, *loc. cit.*; and cf. equation (1)] that a change of one unit in the pH of extraction has the same effect upon the percentage of metal extracted as a ten-fold change in the term $[HDz]_o$. Equation (1) could thus be subjected to a far more stringent test by studying the extractability of zinc from solutions of widely varied acidity. Such a proposal at once introduces a number of complicating factors, since changes in the composition of the aqueous phase due to the presence of buffering agents may be expected to diminish the extractability of zinc should it form competitive complexes with any of the ions present. Quite apart from such possible specific effects, secondary salt effects will affect the final position of partition equilibrium, whilst primary salt effects, and any reduction in the effective concentration of metal ions as a result of complexing, will play a part in affecting the rate at which partition equilibrium is attained.

TABLE 1.

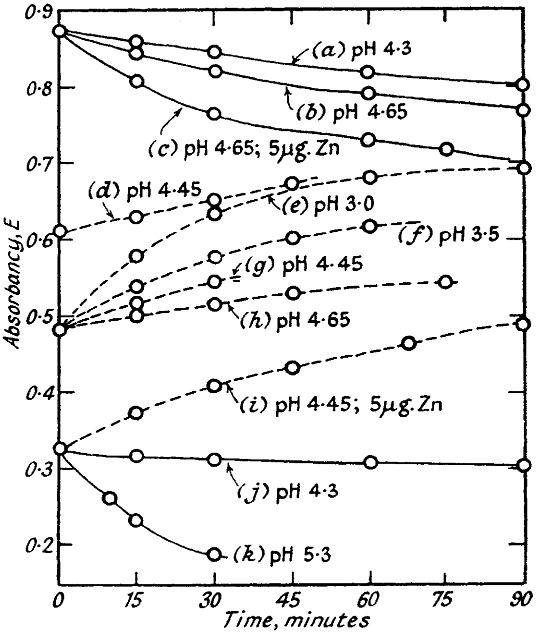
pH	Phase ratio, $H_2O : CHCl_3$, ml.	Zn, μg.	HDz, μg.	*E*	*K*
3·05	10 : 10	11	588, 980	0·29, 0·62	4·7, 3·6
—	5 : 10	5·7	1000	0·93	5·1
3·71	7·5 : 5	5·5,[a] 5·3,[a] 4·9 [b]	150	0·93, 0·77, 0·66	3·25, 2·6, 2·3
3·97	10 : 10	10·0	100, 250, 750	0·3, 1·63, 27	3·4, 3·0, 4·5
—	—	10·5	245, 490	1·44, 7·1	2·8, 3·1

[a] Aqueous phase M with respect to $NaNO_3$. [b] Aqueous phase M with respect to NaCl.

The Attainment of Partition Equilibrium.—In published procedures for the analytical determination of zinc with dithizone, various lengths of time of shaking—generally 1 or 2 minutes—have been allowed for the attainment of partition equilibrium at that pH where the extraction is taken as being quantitative. Kolthoff and Sandell (*loc. cit.*) clearly recognised that this period might be insufficient and prescribed 2 hours for the measurements they made at pH 3—4. That still longer might be necessary at lower acidities can be inferred from data presented by Walkley (*Proc. Austral. Chem. Inst.*, 1942, **9**, 29) and discussed previously (Irving and Williams, *loc. cit.*).

It is clear that the only reliable way of establishing whether partition equilibrium has been truly and finally reached is to approach this point from both sides. We shall speak of a " forward reaction " when zinc dithizonate is formed by shaking together an aqueous buffer containing zinc ions and a solution of dithizone in an immiscible organic solvent, the complex and other species then partitioning between the two phases; the term " back reaction " will be used to describe the processes which ensue when a solution of zinc dithizonate in the organic solvent is shaken with an aqueous buffer whereby reversion takes place to a greater or less extent, zinc ions passing into the aqueous phase and dithizone appearing in the organic phase together with any remaining metal complex. Now any change in the concentration of dissolved zinc dithizonate produces a proportional change in the absorbancy of the organic phase and so permits a simple means of following the kinetics of these processes. From calibration curves (not reproduced here) it was found that the formation and quantitative extraction of 1·06 μg. of zinc (and the concomitant disappearance of the equivalent amount of dithizone) causes a decrease in absorbancy of 0·100 unit under the experimental conditions used and when working with chloroform as a solvent (see p. 365). With carbon tetrachloride as a solvent, or when the Spekker absorptiometer was replaced by a Beckman spectrophotometer, the appropriate factor had to be used. Fig. 1 shows some typical results demonstrating (curves *a* and *b*, *j* and *k*) that the rate of the forward reaction is decreased by lowering the pH of the aqueous phase, the concentration of zinc and dithizone being constant (for each pair). At constant pH, increasing the concentration of dithizone at a fixed zinc concentration (curves *j* and *a*) or increasing the concentration of zinc ion at constant dithizone concentration (curves *b* and *c*) produces the expected increase in the rate of the forward reaction. At constant pH and zinc dithizonate concentration, increase in the concentration of excess dithizone retards the back reaction (curves *g* and *d*), but lowering the pH of the aqueous phase whilst maintaining other factors constant produces a striking increase in the rate of the back reaction (curves *e*, *f*, *g*, and *h*).

FIG. 1. *Factors affecting the rate of approach to partition equilibrium.*



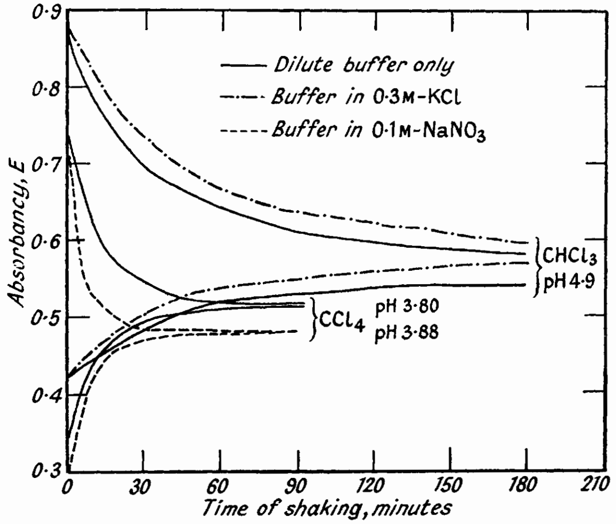
Full curves = forward reaction ; broken lines = back reaction ; 2·5 *μg. of zinc present in all cases except curves* (*c*) *and* (*i*).

It must not be overlooked that the measured rates include both interactions between molecules and ions in solution and the transfer of various species from one phase to the other. That interphase equilibration is not the only rate-determining stage follows from the influence of pH changes; but though these indicate that the concentration of dithizonate ions must play a significant rôle in determining the rate of the forward reaction, our detailed studies of the kinetics are not yet completed. However, since the partition coefficient of dithizone between water and carbon tetrachloride is greater than that between water and chloroform (Irving, Cooke, Woodger, and Williams, *loc. cit.*) there will always be a larger fraction of the total uncomplexed dithizone present in the aqueous phase as dithizonate ion when carbon tetrachloride is used than when a chloroform solution is equilibrated with an aqueous buffer of the same pH. An immediate result of this is to cause the rate of reaction to be greater when using carbon tetrachloride as a solvent for dithizone. Fig. 2 shows that reaction was incomplete in the chloroform–water system at pH 4·9 even after 3 hours' shaking. When carbon tetrachloride was used $1\frac{1}{2}$ hours or even less sufficed to reach equilibrium even at the lower pH of 3·8, and with a smaller concentration of dithizone : at pH 4·9 the reaction is complete within a few minutes.

When, as in most of the measurements with carbon tetrachloride, the curves for the forward and the back reaction actually coincided after a certain time of shaking, the attainment, of equilibrium was not in doubt. In measurements with chloroform, shaking was always continued for long enough to establish the course of the rate curves, and the position of ultimate equilibrium was established by interpolation if necessary; but no results were accepted where the absorbancies of the organic phases in the forward and back reactions differed by more than 5%.

Fig. 2 shows that the effect of a fairly high concentration of chloride ions is to decrease the rate of the forward reaction and to increase that of the back reaction. There is also a change in the final position of equilibrium, the percentage of zinc extracted being reduced from 72·5 to 65%. These effects could well be attributed to the known tendency of zinc ions to form complexes with chloride ions. But caution is necessary in interpreting both such rate and equilibrium measurements, for the presence of a moderate concentration of even an indifferent electrolyte such as sodium nitrate changes the rates of at least the forward reaction (Fig. 2) to an extent greater than can be explained by the small variation in pH and reagent concentration. Here the percentage of zinc extracted happened to be 57% in both cases, so that the effect of the sodium nitrate has been to reduce the effective extraction constant, K, from 98 to 60 (p. 368).

FIG. 2. *Approach to equilibrium from both sides.*



It will be obvious from the foregoing that any attempts to correlate and interpret variations of the percentage of zinc extracted with change of pH can only be justified with data obtained at equilibrium and with due regard to the composition of the buffers employed. Entirely misleading pictures would be obtained, if, *e.g.*, measurements with chloroform solutions of dithizone were made after only 15 minutes' shaking. Nevertheless, data obtained after even 2 minutes' shaking and shown in Table 2 confirm the effect of chloride ion in reducing at least the *rate* of extraction of zinc and demonstrate the even greater effect of phosphate ions and the advisability of omitting them from buffer

TABLE 2. *The effect of chloride and phosphate ions upon the extractability of zinc from phosphate buffers at* pH 6·7.

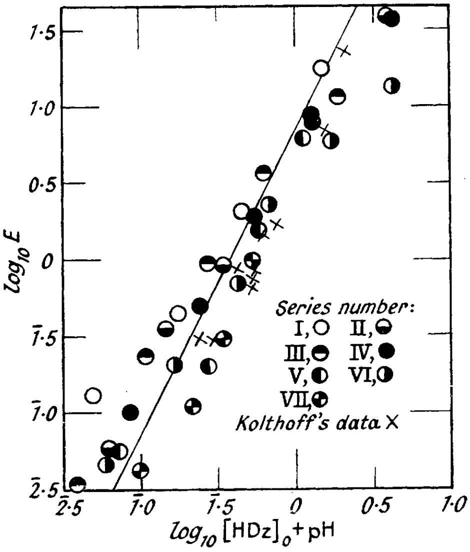
Zinc taken, μg.	4	8	12	16	20
KCl, M	0·2	0·4	0·6	0·8	1·0
Zn, %, extracted in 2 min. from					
(*a*) M-Na_2HPO_4	20	19	14	13	10
(*b*) 0·1M-Na_2HPO_4	48	46	47	45	40

mixtures used in measurements of the extractability constant K: but these data are valueless as indicating the possible position of extraction equilibrium.

A study was next undertaken of the effect of pH upon the equilibrium percentage of zinc extracted by dithizone solutions of the same initial strength from aqueous buffers of different composition. Of the family of curves which resulted, that obtained for M/200 phthalate buffers formed the left-hand member, indicating the greatest extent of extraction at any pH and the least degree of complexing with zinc ions. To its right lay curves for M/10- and M/2-phthalate, and M/2-acetate, -tartrate, and -citrate in that order: at any given pH more zinc was extracted from an acetate buffer than from a phosphate buffer of the same molarity.

The Extraction Constant for the Zinc–Dithizone–Chloroform System.—In this main part of the work the position of equilibrium was determined for a variety of acidities and varying values of $[HDz]_o$. The same total weight of zinc (5 μg.) was present in each case and

FIG. 3. *Equilibrium data obtained from the extraction of zinc by solutions of dithizone in chloroform.*

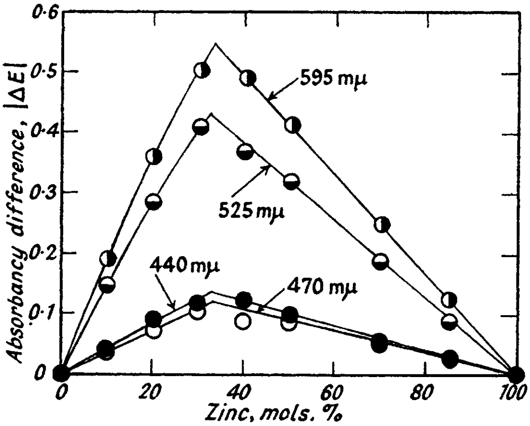


M/200-phthalate buffers were employed throughout, equilibrium being approached as usual from both sides. In the first series of experiments the total amount of dithizone in the system amounted to 160 μg., and this was progressively reduced to 146, 90, 70, 60, 48, 32, and 15 μg. in Series II to VIII. In Series VII and VIII the initial concentration of dithizone was insufficient to react with all the zinc taken (5 μg. of Zn ≡ 40·3 μg. of HDz) so that complete extraction could never be achieved. Furthermore, equilibrium could not be approached by the back reaction; but even without this criterion the low percentage of zinc extracted showed that partition equilibrium was not being reached even after 4—5 hours' shaking. The possibility of the formation of a water-soluble zinc–dithizone complex (*q.v.*) should also be taken into account.

Series I to VI at once provide sets of values of the parameters E, pH, and $[HDz]_o$ which can be used to test equation (1*a*). Fig. 3 shows experimental values of $\log_{10} E$ plotted against $\log_{10} [HDz]_o + pH$, together with a straight line of slope $n = 2$ corresponding to a complex of formula $ZnDz_2$. The radius of the circles is not intended to indicate the precision of the measurements, which falls off very rapidly as the percentage of extraction falls outside the range 50 to 95%. Agreement with theory is satisfactory in view of the range of extractabilities and acidities covered, and the scatter is least, as might be expected, in the neighbourhood of $\log_{10} E = 1$ (50% extraction). Values obtained by Kolthoff and Sandell (*loc. cit.*) are indicated by crosses in Fig. 3, and the fact that they all correspond to lower extractabilities than we have found might possibly be attributable to equilibrium not having been attained, although the fact that they were obtained with buffers of different and higher salt content must not be overlooked (cf. p. 358). The greater self-consistency of their measurements is due in large part to the limited range (pH 3·05—3·97) covered. If we accept the formula of the complex as $ZnDz_2$ we obtain $K = 8 \pm 0{\cdot}8\%$ from our data, which may be compared with the average value $3{\cdot}3 \pm 0{\cdot}3\%$ obtained if equal weight is given to all Kolthoff and Sandell's values. On the other hand, the data of Fig. 3 could justifiably be considered as conforming more satisfactorily with a line of slope as low as 1·7 though an objective estimate of the position of this " best straight line " is difficult in view of the low precision of data corresponding to high and low values of $\log_{10} E$.

There can, however, be little doubt as to the formula of the red zinc–dithizone complex which is extracted into the organic phase. That the pure solid conforms to the expected composition is shown by Fischer's analysis (*Annalen*, 1882, **212**, 316) and those of our own specimens. The formula is supported by measurements incidental to setting up calibration curves (p. 365), and is finally established by a spectrophotometric study of mixtures of zinc and dithizone in a monophase of chloroform, alcohol, and water, using the method of continuous variations described by Job and modified by Vosburg and Cooper (*J. Amer. Chem. Soc.*, 1941, **63**, 437). The ordinates in Fig. 4 measure the difference, ΔE, at each of four selected wave-lengths, between the measured absorbancy and that calculated on the assumption that no complex formation has taken place. This difference reaches its maximum value when the mole-fraction is 0·33 corresponding to a molecular ratio Zn : HDz of 1 : 2. No other absorbing species appear to be formed under these experimental conditions.

FIG. 4. *The formula of zinc dithizonate—Job's method of continuous variations.*



(*Values of* ΔE *are negative for* 595 *and* 440 *mμ, and positive for* 525 *and* 470 *mμ.*)

Even though the formula, $ZnDz_2$, of the extracted species is no longer in doubt, a non-integral slope for the plot of log E against log $[HDz]_o$ + pH (Fig. 3) could nevertheless arise from the following considerations. If we accept the current view that the formation of a complex proceeds through the stepwise addition of ligands, we must extend our treatment of the fundamental equilibrium to include the following species in the aqueous phase: $Zn^{++} + Dz^- \rightleftharpoons ZnDz^+$; $ZnDz^+ + Dz^- \rightleftharpoons ZnDz_2$. These equilibria are governed by stability constants defined by $k_1 = [ZnDz^+]/[Zn^{++}][Dz^-]$ and $k_2 = [ZnDz_2]/[ZnDz^+][Dz^-]$, whilst the amphoteric character of the zinc ion can be considered in terms of the stability constants $k_n{}^h = [Zn(OH)_n]/[Zn(OH)_{n-1}][OH^-]$. We can now write (deferring consideration of activity coefficients for the time being)

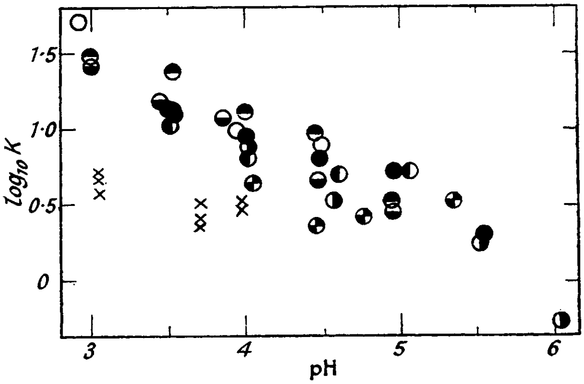
$$\begin{aligned} E &= [ZnDz_2]_o/([Zn^{++}]_w + [ZnDz^+]_w + [ZnDz_2]_w + [ZnOH^+]_w{}^+ \ .\ .\ .\ .\ ) \\ &= ([ZnDz]_o/[Zn^{++}]_w)/(1 + k_1[Dz^-] + k_1k_2[Dz^-]^2 + k_1{}^h[OH^-]\ .\ .\ .) \\ &= \frac{K[HDz]_o{}^2}{\{H\}^2}\Bigg/\left(1 + k_1p_rK_r\frac{[HDz]_o}{\{H\}} + k_1k_2p_r{}^2K_r{}^2\frac{[HDz]_o{}^2}{\{H\}^2} + \frac{k_1{}^hK_w}{\{H\}} + \text{etc.}\right) \end{aligned}$$

Taking logarithms and rearranging, we have

$$\log_{10} K \text{ (calc.)} = \log_{10} E\text{(expt.)} - 2(\log_{10} [\mathrm{HDz}]_o + \mathrm{pH})$$
$$= \log_{10} K - \log_{10} (1 + k_1 ax + k_1 k_2 a^2 x^2 + k_1{}^h K_w/\{\mathrm{H}\} + \text{etc.}) \quad (4)$$

where the variable $x = [\mathrm{HDz}]_o/\{\mathrm{H}\}$, and the constant a is given by $\log_{10} a = \log_{10} p_r K_r = \mathrm{pH}_{\frac{1}{2}}$. It follows that the value of the extraction constant calculated according to equation (1) may, depending on the values of k_1, k_2 and $k_n{}^h$ (*i.e.*, on the extent to which water-soluble complexes participate in the equilibria), be found to vary with the terms $[\mathrm{HDz}]_o$ and pH—in short with the conditions of extraction. In our experiments the latter parameter was subject to the greater variation, and, as may be inferred from equation (4), the calculated extraction constants would then decrease with increasing pH. This prediction agrees with the trend of our experimental data shown plotted against pH in Fig. 5; the trend of Kolthoff and Sandell's value is in the same direction but the agreement must not be over-emphasised in view of the small range of acidities they cover. If we insert numerical values for $p_r K_r$ ($2{\cdot}63 \times 10^{-11}$; Irving *et al.*, *loc. cit.*) and $k_1{}^h K_w$ ($2{\cdot}45 \times 10^{-10}$; Latimer, "Oxidation Potentials," New York, 1938) into equation (4), it is obvious that the hydrolysis of the zinc ion to give ZnOH^+ is not sufficiently extensive over the range of acidities studied to explain the trend of our results, and it proved impossible to assign consistent values to k_1 and k_2 though the former appeared to lie in the range $10^{10} < k < 10^{12}$.

FIG. 5. *The variation of* $\log_{10} K$ *for chloroform with* pH.



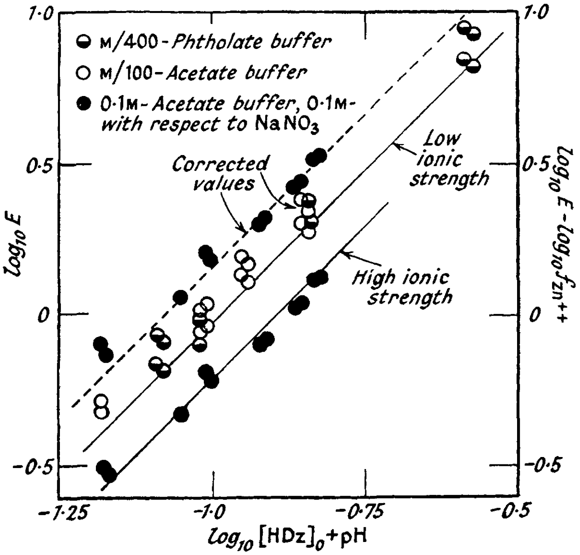
(*The symbols employed have the same significance as in Fig.* 3.)

The Extraction Constant for the Zinc–Dithizone–Carbon Tetrachloride System.—Since the factor $a = p_r K_r$ for carbon tetrachloride is some 50 times greater than that for chloroform, we should expect a larger dependence of the experimental values of the extraction constant K upon the conditions of measurement. An additional reason for studying this system is provided by Buch's data (*Finska Kemist. Medd.*, 1944, **53**, 25) for the extraction of zinc from acetate buffers from which Sandell (*loc. cit.*) calculates $K_{\mathrm{CCl_4}} = 4$, a value almost identical with that found by him in chloroform (see p. 358). This is most surprising in view of the known dependence of K upon parameters characteristic of the solvent, and it conflicts with the fact that the optimum pH for the extraction of a metal with a solution of dithizone in carbon tetrachloride appears without exception to lie below that of the corresponding value for chloroform.

Although preliminary measurements had shown that equilibrium was attained more rapidly when carbon tetrachloride was substituted for chloroform (see p. 359 and Fig. 2), partition equilibrium was nevertheless invariably approached from both sides and, in view of the reduced precision of measurements at high or low values of E, the percentage of zinc extracted was kept within the range 20—90%. Excellent agreement was obtained between preliminary measurements where the forward and back reactions were investigated in separate experiments (p. 368), but in the final measurements both forward and back reactions were conducted simultaneously. The variation with pH of the percentage of zinc extracted was found to be the same whether the aqueous buffer was M/200-phthalate or M/100-acetic acid–sodium acetate, and Fig. 6 shows the plot of log E against log $[HDz]_o$ + pH together with a line of slope 2. The agreement with theory is most satisfactory, and we find $K = 97 \pm 2$. When these buffers of low ionic strength are replaced by one for which $\mu \sim 0{\cdot}1$ due to a constant background of 0·1M-sodium nitrate, the data, though conforming excellently to a line of slope 2 (Fig. 6) now lead to the value $K = 66 \pm 2$. Despite the apparent disagreement, there is no doubt that K_{CCl_4} is greater than K_{CHCl_3} by a factor of about 10; this is compatible with qualitative observations but in marked disagreement with Buch's earlier data.

If, however, the derivation of equation (1) is carried through by using activities in place of concentration terms, and thermodynamic constants denoted by adding the superscript T to symbols previously used, then, by making the appropriate redefinitions where necessary, it can readily be shown that

FIG. 6. *The effect of ionic strength upon the extraction constant for the system zinc–dithizone–carbon tetrachloride and water.*



(*The right-hand ordinate scale applies to the broken line.*)

$$E = K^T f_{Zn^{++}} \{HDz\}^2/\{H\}^2$$

or $$\log_{10} E - \log_{10} f_{Zn^{++}} = \log_{10} K^T + 2(\log_{10} \{HDz\}_o + pH) \quad . \quad . \quad . \quad (5)$$

where $f_{Zn^{++}}$ is the activity coefficient of the zinc ion and $K^T = (p_r^T K_r^T)^2/(p_c^T K_c^T)$. On assuming that $[HDz]_o = \{HDz\}_o$, and that $f_{Zn^{++}}$ equals $f_\pm$, the mean activity coefficient for zinc sulphate, and making the appropriate calculations, all the partition data now conform to a single line of slope 2 (Fig. 6, broken line). In effect, points corresponding to media of low ionic strength are displaced vertically upwards by 0·05 to 0·1 logarithmic unit, whilst those for the medium of high ionic strength need correction to a much greater extent of 0·4 unit on the $\log_{10} E$ scale. From the intercept at $\log_{10} E = 0$, we have $\log_{10} K^T = 2{\cdot}11 \pm 0{\cdot}01$, or $K_{CCl_4} = 130$ ($\mu = 0$) with a standard deviation of ± 4.

The work with carbon tetrachloride was not pursued with buffers of pH > 4 where materially lower concentrations of dithizone would have had to be used to keep within a convenient range of extractabilities; but over the admittedly limited range explored there is not the slightest evidence of any trend in the values of K with increasing pH such as had been noted in the chloroform system. In this system Kolthoff and Sandell used "biphthalate buffers, of pH 3 and 4, according to Clark and Lubs." Assuming these to have been 0·05M, we can estimate the value $K_{\text{CHCl}_3} = 9$ ($\mu = 0$), which compares very favourably with the value $K^T = 11$ obtained by applying the appropriate activity correction to our data at the same pH. Since, as a result of increasing ionisation, the ionic strength of our phthalate buffers increased as the pH was increased, the activity correction to be applied to the data at high pH values becomes increasingly significant, and it may well be that this accounts for the major part, if not the whole, of the drift of values shown in Fig. 5. Unfortunately, the exact composition of these buffers (which were prepared by addition of arbitrary amounts of alkali to stock dilute phthalate buffer—the measurement of pH being deferred until after partition equilibrium had been attained) is not available, and we cannot now subject this hypothesis to a quantitative test. There now remains, however, no very definite evidence for the existence of a water-soluble complex such as $ZnDz^+$, and although further progress could be made by more precise equilibrium studies of extraction from media of accurately known ionic strength, it is clearly desirable to refine the analytical methods available for determining the concentration of the various species comprising the equilibrium mixtures. Particularly valuable information would result from an objective determination of the amount of dithizone present as the species HDz, Dz^-, $ZnDz^+$, and $ZnDz_2$ in the *aqueous* phase, and to this end the synthesis of a radioactive reagent with suitably labelled atoms has been undertaken.

EXPERIMENTAL

Materials and Technique.—Precautions customary in work with dithizone were scrupulously observed. All solvents, buffers, reagents, and glassware were freed from trace metals in the customary way (*J.*, 1949, 537, 541, 1847). Partition equilibrium was approached by shaking organic and inorganic solutions in 125-ml. Pyrex stoppered funnels in the earlier work with chloroform, but with carbon tetrachloride stoppered Pyrex test-tubes were employed exclusively and phase separation was assisted if necessary by centrifugation.

The Standard Mixed-colour Calibration Curves for Zinc Dithizonate.—Mixtures of x ml. of zinc solution (1 μg. per ml. of acetate buffer) with $(10 - x)$ ml. of an acetate buffer of pH 7·5, both saturated with chloroform, were shaken for 5 minutes with a solution of dithizone in chloroform previously saturated with water by equilibration with 0·1N-hydrochloric acid. After standing to permit of phase separation the organic layer was separated through a plug of cotton wool (previously freed from trace-metals) and after rejection of the first portions it was used to fill a 1-cm. cell of a Spekker absorptiometer which had been warmed slightly on the lamp-house to avoid any danger of spurious high absorbancies resulting from the separation of water droplets had the organic phase become supersaturated following a drop in temperature after equilibration. The absorbancy (optical density) of the initial dithizone solution, E_o, and that of each mixture of zinc dithizonate and excess dithizone, E_m, was measured by use of the tungsten lamp and Ilford orange filter No. 607. The plot of absorbancy against the weight of zinc taken was linear over the range 0—6 μg., the extraction of 1 μg. of zinc corresponding to a decrease in absorbancy of $0{\cdot}094_5$. From previous work (Irving, Risdon, and Andrew, *J.*, 1949, 537) on the relation between absorbancy and the concentration of chloroform solutions under these conditions, we calculate that 7·2 μg. of zinc have reacted with 57 μg. of dithizone, corresponding to a molecular ratio Zn : HDz = 1 : 1·97. The calibration curve for zinc with solutions of dithizone in carbon tetrachloride was carried out by use of an 0·05M-acetate buffer of pH 5·33, and 30 minutes' shaking. The following data are typical, but fresh calibration curves were repeated at intervals to check the purity of the dithizone used and to ensure that there had been no deterioration or change in the transmittancy of the optical filter.

Zn taken, μg.	0	1·0	1·5	2·0	3·0	4·0	5·0	6·0
E_m	0·665	0·570	0·535	0·488	0·403	0·318	0·245	0·150

On the average 1 μg. of zinc reduces the absorbancy by 0·085 unit, indicating for the dissolved species the formula $ZnDz_{2{\cdot}04}$.

Kinetic and Equilibrium Studies.—" Forward " reactions were studied by shaking aqueous buffers containing known amounts of zinc with dithizone solutions of known initial concentration (as measured by E_o) for the desired length of time. After separation of the phases, the pH of the aqueous phase was measured with a Cambridge pH-meter, and the absorbancy of the organic phase determined as above. The concentration of excess dithizone, $[\mathrm{HDz}]_o$, is proportional to E_m, whilst the amount of zinc extracted is obtained from $E_o - E_m$ and the factor obtainable from the calibration curves. "Back" reaction mixtures were prepared by extracting known amounts of zinc quantitatively from aqueous solution under the conditions used for preparing the calibration curves (see above). The initial composition in terms of $[\mathrm{ZnDz_2}]$ and $[\mathrm{HDz}]_o$ followed from the amount of zinc and dithizone taken, but it was invariably checked by measurements of the changes in absorbancy and sometimes by a complete reversion of the metal complex by prolonged shaking with 0·1M-hydrochloric acid. Equilibration was carried out on a mechanical shaker operating at 150 cycles per minute, and in kinetic measurements a number of identical mixtures were made up and set shaking simultaneously, one test-tube (or funnel) being removed at suitable intervals for the analysis of its contents. The temperature was 25° ± 3°. Blanks were run in every case.

Factors Affecting the Rate of Approach to Equilibrium in the System Zinc–Dithizone–Water and Chloroform.—The values of E_m obtained in some typical experiments are given below. (All measurements with chloroform solutions were carried out by R. J. P. W.)

Expt. No.	pH	Time, min. : 0	15	30	60	90	150
1	4·30	0·325	—	0·315	0·310	0·305	—
2	4·30	0·870	—	0·845	0·820	0·800	—
3	4·65	0·870	—	0·820	0·790	0·765	—
4	5·30	0·325	0·215	0·180	—	—	—
5	4·65	3·75	3·59	3·56	—	—	—
6	4·60	0·750	0·680	0·645	0·615	0·590	0·570
7	3·00	0·480	0·585	0·635	0·680	0·695	—
8	3·50	0·480	0·540	0·575	0·615	—	—
9	4·65	0·480	0·498	0·515	0·540	—	—
10	4·45	0·30	0·35	0·38	0·43	0·47	0·51
11	4·45	0·48	0·515	0·545	—	—	—
12	4·45	0·110	0·130	0·150	0·170	—	—

The amount of zinc taken (as zinc ion or zinc dithizonate) was 2·5 µg. in all experiments save Nos. 6 and 10, where 5·0 µg. were used; Nos. 1—6 are forward, Nos. 7—12 are back reactions. The organic phase of experiment No. 5 was diluted 5-fold before measurement of absorbancy.

The Effect of Potassium Chloride upon the Rate of Extraction of Zinc.—A mixture of 2 ml. of zinc sulphate solution (4·8 µg. Zn), 3 ml. of M-potassium chloride (or distilled water), and 5 ml. of 0·004M-phthalate buffer of pH 4·9 was shaken for varying lengths of time with 10 ml. of a solution of dithizone in chloroform ($E_o = 0·875$). Simultaneous measurements were made of the rate of reversion of 10 ml. of zinc dithizonate–dithizone mixtures in chloroform (containing the same total amount of zinc and dithizone as above) on shaking with an aqueous phase containing 2 ml. of water in place of the zinc solution.

	No KCl present					0·3M-KCl present				
Time, min.	0	30	60	90	180	0	30	60	90	180
Zn, % extracted :										
(i) Forward reaction	0	14	52	59	71	0	32	47	52	62
(ii) Back reaction	100	86	79	78	74	100	83	75	73	68

The Effect of Potassium Chloride on the Position of Equilibrium.—Similar measurements were carried out at different acidities, the pH of the phthalate buffers being adjusted to the desired values by the addition of 0·02M-hydrochloric acid (or ammonia); $E_o = 0·738$.

pH	1·8	3·5	4·0	4·6	4·9	5·5	6·5
Zn, %, extracted :							
(i) No KCl	0	6	8	40	66	91	100
(ii) 0·3M-KCl	0	8	18	58	78	96	100

The Effect of Potassium Chloride on the Rate of Reaction in Phosphate Buffers.—In order to see whether the effect of potassium chloride and phosphate ions on the extraction of zinc was due to specific complexing and/or to an activity effect it was necessary to produce buffers of the same pH but widely different concentration. Solutions of 1·0M- and 0·1M-disodium hydrogen phosphate were prepared, together with similar buffers which were M with respect to potassium chloride and contained 2µg./ml. of zinc. By adding drops of 1·0M-hydrochloric acid, the pH was adjusted empirically to the value 6·70 in each case, the four buffer solutions now having the following composition (in addition to the above small volume of acid) :

	Concn. of Na_2HPO_4, M	Concn. of KCl, M	Zn, μg./ml.
(i)	1	0	0
(ii)	1	1	2
(iii)	0·1	0	0
(iv)	0·1	1	2

Mixtures of x ml. of (i) with $(10 - x)$ ml. of (ii) contained varying amounts of potassium chloride in M-disodium hydrogen phosphate buffers of pH 6·7. These and similar mixtures solutions (iii) and (iv) were shaken for two minutes only with an equal volume of dithizone solution of $E_0 = 0{\cdot}831$. The results are shown in Table 2 (p. 360).

The Extraction Constant for the Zinc–Dithizone–Chloroform System.—Preliminary experiments having indicated the time necessary to reach equilibrium, simultaneous measurements were made of the forward and back reactions with mixtures so designed that at equilibrium both organic and both aqueous phases should be identical in composition in the two cases. If the two values of E_m differed by more than 5% the experiment was repeated with a longer time of shaking. When a very high concentration of dithizone was used (Series I) the absorbancy was too high for direct measurement, and after equilibrium had been attained the zinc dithizonate in the organic layer was " reverted " into 10 ml. of 1M-hydrochloric acid and after neutralisation and buffering to pH 8·0 determined in the usual way. In Series VII and VIII the amount of dithizone taken was less than that sufficient to combine with all the zinc. No equivalent mixture could thus be made up for the back reaction and the data given refer only to the forward reaction.

Factors Affecting the Rate of Approach to Equilibrium in the System Zinc–Dithizone–Carbon Tetrachloride–Water.—All measurements with carbon tetrachloride solutions were carried out by C.F.B., stoppered test-tubes being used exclusively in preference to separating funnels. The extent to which concentration changes occurred during long periods of shaking was investigating by taking a mixture of at least 10 ml. of water and a similar volume of carbon tetrachloride and placing it in a Pyrex test-tube (20 × 3 cm.) with a B 24 ground-in stopper. The tube was stoppered and weighed after being shaken for 0, ½, 1½, and 4 hours on a Kahn shaking machine at 150 cycles per minute. With nine different tubes the largest decrease in the weight of liquid after 4 hours was 0·1% and the average loss was only 0·002%.

Series No.	pH	$\log_{10}$ [HDz]$_o$	$\log_{10} E$	$\log_{10} K$
I	2·58	$\bar{5}$·7943	$\bar{2}$·0044	1·27
	2·93	$\bar{5}$·7830	$\bar{1}$·1264	1·70
	3·50	$\bar{5}$·7608	$\bar{1}$·6526	1·13
	3·95	$\bar{5}$·7157	0·3174	0·99
	4·50	$\bar{5}$·6782	1·2520	0·90
	5·00	$\bar{5}$·6710	$>3{\cdot}0$	—
II	2·53	$\bar{5}$·7582	$<\bar{3}{\cdot}0$	—
	3·00	$\bar{5}$·7471	$\bar{2}$·8090	1·41
	3·45	$\bar{5}$·7253	$\bar{1}$·5229	1·18
	3·85	$\bar{5}$·6956	$\bar{1}$·9513	0·86
	4·48	$\bar{5}$·6371	0·8862	0·65
	4·96	$\bar{5}$·6212	1·5911	0·43
III	2·53	$\bar{5}$·5436	$\bar{2}$·1023	1·96
	3·00	$\bar{5}$·5387	$\bar{2}$·5906	1·51
	3·52	$\bar{5}$·5056	$\bar{1}$·3979	1·35
	4·00	$\bar{5}$·4369	0·0000	1·13
	4·45	$\bar{5}$·3552	0·6021	0·99
	4·96	$\bar{5}$·3161	1·0910	0·54
IV	3·52	$\bar{5}$·4113	$\bar{2}$·9899	1·13
	4·03	$\bar{5}$·3515	$\bar{1}$·6944	0·93
	4·48	$\bar{5}$·2546	0·2900	0·82
	4·96	$\bar{5}$·1481	0·9495	0·73
	5·52	$\bar{5}$·1103	1·5736	0·31
V	2·47	$\bar{5}$·3663	$\bar{2}$·1522	2·47
	3·50	$\bar{5}$·3552	$\bar{2}$·7392	1·03
	4·02	$\bar{5}$·2908	$\bar{1}$·4324	0·81
	4·60	$\bar{5}$·1481	0·2071	0·71
	5·05	$\bar{6}$·9990	0·8067	0·72
VI	3·52	$\bar{5}$·2546	$\bar{2}$·6630	1·10
	4·02	$\bar{5}$·2046	$\bar{1}$·3265	0·88
	4·58	$\bar{5}$·0689	$\bar{1}$·8347	0·54
	4·96	$\bar{6}$·8928	0·3680	0·67
	5·52	$\bar{6}$·7379	0·7812	0·26
	6·03	$\bar{6}$·6332	1·1167	$\bar{1}$·79
VII	4·05	$\bar{6}$·9342	$\bar{2}$·6232	0·65
	4·45	$\bar{6}$·8928	$\bar{1}$·0458	0·36
	4·76	$\bar{6}$·7679	$\bar{1}$·4777	0·42
	5·35	$\bar{6}$·3700	$\bar{1}$·9948	0·56
	5·98	$\bar{7}$·5908	0·2432	1·10
VIII	4·20	$\bar{6}$·7379	$\bar{2}$·1822	0·31
	5·10	$\bar{6}$·4369	$\bar{1}$·2989	0·22
	5·80	$\bar{6}$·2046	$\bar{1}$·5324	$\bar{1}$·51
	6·15	$\bar{6}$·0689	$\bar{1}$·5941	$\bar{1}$·15
	7·00	*	$\bar{1}$·6990	—

* Indicates that there was no measurable excess of dithizone.

The Effect of Change of Ionic Strength on the Rate of Extraction of Zinc.—In Series A, mixtures of 1 ml. of stock zinc sulphate solution (5 μg. of Zn/ml.), 2 ml. of 0·5M-sodium nitrate, 5 ml. 0·2M-acetic acid–sodium acetate buffer of pH 3·88, and 2 ml. of metal-free water were shaken with 10 ml. of a solution of dithizone in carbon tetrachloride of $E_0 = 0{\cdot}735$ when studying the forward reaction. For the back reaction 10 ml. of a solution of zinc dithizonate in carbon tetrachloride (5 μg. of Zn) were shaken with 2 ml. of 0·5M-sodium nitrate, 5 ml. of 0·2M-buffer, and 3 ml. of water. In Series B the aqueous phase was in each case a 0·02M-acetic acid–sodium acetate buffer of pH 3·80, containing 5 μg. of Zn for the forward reaction only; $E_0 = 0{\cdot}750$. The results are plotted in Fig. 2.

Time of shaking, min.		0	10	20	60	90
Zn, %, extracted :						
Series A :	(i) forward	0	48	55	57	57
	(ii) backward	100	68	60	58	57
Series B :	(i) forward	0	40	50	54	56
	(ii) backward	100	71	62	60	58

The Extraction Constant for the Zinc–Dithizone–Chloroform System.—A set of equilibration experiments at various pH values was carried out by using aqueous phases of "high" ionic strength of the composition used in Series A above. The forward and the back reactions were studied in random order and with different samples of reagents. The following results indicate the degree of concordance obtainable in such measurements :

	Zn extracted, % :			
pH	forward	backward	$\log_{10} E$	$\log_{10}\,[HDz]_o$
3·56	—	32·4	−0·319	−4·68
3·65	—	40·9	−0·168	−4·68
3·86	53·3, 54·0	—	0·064	−4·76
3·88	—	56·7	0·117	−4·77
3·96	—	62·4	0·220	−4·78
4·06	73·1, 72·1	—	0·423	−4·82
4·22	81·9, 80·2	—	0·630	−4·87

The definitive experiments were carried out with mixtures for forward and back reaction being equilibrated simultaneously. In Series C the aqueous phase comprised 0·1M-acetic acid–sodium acetate buffers made 0·1M with respect to sodium nitrate; in Series D it was 0·02M-acetic acid–acetate buffer; and in Series E it was a 0·0025M-phthalate buffer.

		Forward reaction			Backward reaction		
	pH	$-\log_{10} E$	$-\log_{10}\,[HDz]_o$	$-\log_{10} f_{Zn^{++}}$	$-\log_{10} E$	$-\log_{10}\,[HDz]_o$	$-\log_{10} f_{Zn^{++}}$
Series C	3·47	0·502	4·65	0·391	0·530	4·64	0·391
	3·62	0·33	4·67	0·393	0·33	4·67	0·393
	3·69	0·19	4·70	0·395	0·22	4·69	0·395
	3·80	0·10	4·72	0·398	0·09	4·71	0·398
	3·88	−0·02	4·74	0·400	−0·04	4·73	0·400
	3·93	−0·11	4·76	0·404	−0·12	4·75	0·404
Series D	3·50	0·33	3·78	0·05	0·33	3·78	0·05
	3·72	0·04	3·74	0·06	0·05	3·72	0·05
	3·82	−0·12	4·01	0·07	−0·10	3·99	0·07
	3·96	−0·31	4·34	0·07	−0·27	4·30	0·07
Series E	3·60	0·160	4·69	0·095	0·188	4·68	0·098
	3·68	0·084	4·70	0·094	0·090	4·70	0·101
	3·94	−0·277	4·78	0·093	−0·269	4·78	0·101
	4·28	−0·845	4·87	0·095	−0·827	4·85	0·103

Spectrophotometric Studies on the Composition of the Zinc–Dithizone Complex.—Measurements had to be made in a homogeneous phase in which zinc salts, dithizone, and zinc dithizonate were all freely soluble, and a monophase composed of 20% chloroform, 10% water, and 70% ethyl alcohol was found to be most suitable. In this medium the absorption spectrum of dithizone differs little from that in chloroform alone save that the maxima are located at 595 mμ (principal) and 440 mμ (subsidiary). Zinc dithizonate gave a single band centred at 525 mμ, and dithizonate ions (obtained by adding alkali to the monophase) had $\lambda_{max.} = 470$ mμ. These and the following measurements were made with a Beckman Model D.U. Spectrophotometer and 1·00-cm. Corex cells.

A strong solution of pure dithizone in chloroform was next prepared and its concentration found to be $1{\cdot}17 \times 10^{-4}$M by measuring the absorbancy after 5-fold dilution with pure chloroform and interpolating from a standard curve. A solution of zinc ions of exactly twice this concentration was then prepared by diluting a suitable volume of a concentrated stock solution of zinc sulphate with M/200-phthalate buffer, the pH being adjusted simultaneously to 5·7—5·8. The mixtures required for Job's method (*loc. cit.*), in which the relative proportions of zinc and dithizone vary but the same *total* concentration in the monophase of $2{\cdot}34 \times 10^{-5}$M is maintained, were prepared by mixing ($20 - 2x$) ml. of dithizone solution, $2x$ ml. of pure chloroform, ($10 - x$) ml. of aqueous M/200-phthalate buffer of pH 5·7—5·8, and x ml. of the standard $2{\cdot}34 \times 10^{-4}$M-zinc solution. Absorbancies measured at four wave-lengths are given below:

	Absorbancy, measured at mμ.			
x, ml.	440	470	525	595
0·0	0·362	0·285	0·260	0·850
1·0	0·286	0·293	0·380	0·575
2·0	0·200	0·298	0·492	0·318
3·0	0·137	0·304	0·593	0·090
4·0	0·097	0·260	0·525	0·020
5·0	0·085	0·230	0·450	0·011
7·0	0·055	0·140	0·268	0·007
8·5	0·025	0·067	0·130	0·003
10·0	0·000	0·000	0·000	0·001

Final optical densities were established almost instantaneously in the monophase so that complex formation is clearly greatly accelerated under these conditions.

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