TABLE I

HEAT CAPACITY OF GASEOUS PERFLUOROCYCLOBUTANE (C_4F_8) SUMMARY OF RESULTS

Pressure, atm.	10.00°	50.00°	90.00°
	C_p, cal. mole^{-1} degree^{-1}		
1.50		39.93	42.43
1.00	37.03	39.69	42.28
0.67	36.74		
.50		39.46	42.16
.33	36.47		
C_p°, obsd.	36.19	39.23	42.01
C_p°, spec.[a]	36.80	39.82	42.56
$\Delta C_p/\Delta P$, cal. mole^{-1} deg.$^{-1}$ atm.$^{-1}$	0.84	0.47	0.28

[a] From assignment by H. H. Claassen, *J. Chem. Phys.*, **18**, 543 (1950).

"Freon C318" are 0.22, 0.16 and 0.13. The equation of state referred to is

$$PV = RT + (0.0019425T - 2.570)/V + (0.02878 - 0.00002247T)/V^2 \quad (6)$$

where P is in p.s.i.a., T is in degrees Rankine, and V is in ft.^{3}/lb.

The determination of the value of the constant b awaits precise vapor density measurements at low pressure.

Acknowledgments.—The author wishes to thank Mr. Howard Flieger, Mr. Joseph Ratti and Mr. John Wicklund for assistance with the experimental work and with the calculations. He is indebted to the E. I. du Pont de Nemours Co. and to the Minnesota Mining and Manufacturing Company for gifts of samples.

WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Analysis of Lead Dithizonate by the Method of Continuous Variations[1]

BY STANCIL S. COOPER AND JAMES O. HIBBITS[1b]

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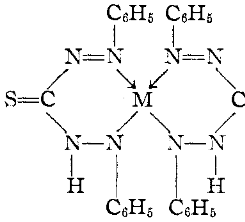
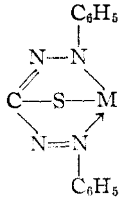
The formulas PbDz and $PbDz_2$ have been proposed for the complex between divalent lead and dithizone. All previous analyses of this complex have employed photometric calibration curves based upon weighed amounts of dry reagent; however doubt exists as to the purity of dithizone in the dry form. Purified dithizone–carbon tetrachloride solutions, of concentrations established by molar extinction coefficient data, were used in this investigation. Purity was checked by a criterion based upon the optical density at 620 and 450 mμ. The formula $PbDz_2$ was confirmed by Job's method of continuous variations. The significance of the relative magnitudes of the molar extinction coefficients necessary to the method is presented for the general case.

Since its introduction by Fischer[2] in 1929, diphenylthiocarbazone ("dithizone," Dz) has been applied extensively as a reagent for the determination of small amounts of lead. The structure of the divalent lead–dithizone complex at *p*H 8–10 was proposed by Fischer to be $PbDz_2$ (I), involving the keto form of the reagent.



I, keto complex



II, enol complex

Liebhafsky and Winslow[3] investigated the structure of the complex experimentally, and concluded the formula to be PbDz (II), involving the enol form of the reagent. The method employed was to extract known amounts of lead into a carbon tetrachloride–dithizone phase, from which the excess reagent was removed by extraction with an aqueous solution of potassium cyanide; the complex left in the organic phase was destroyed with dilute perchloric acid, and the dithizone liberated was determined photometrically by reference to a standard curve. Clifford,[4] in an attempt to resolve the disagreement, pursued a line of investigation similar to that of Liebhafsky and Winslow. Solutions of dithizone in carbon tetrachloride were shaken with a twofold excess of lead, and the dithizonate formed was extracted into the organic phase. Portions of the dithizonate solution were analyzed for lead electrolytically. Other portions of the same solutions were shaken with dilute acid to destroy the dithizonate, which reverted to the green dithizone color, and the amount of dithizone equivalent to the lead present was determined photometrically with reference to a calibration curve. As a result of this work, Clifford arrived at the formula $PbDz_2$.

The formula $PbDz_2$ was also obtained by Irving[5] through his "reversion" procedure.

These methods suffer from the difficulty that a calibration curve, based upon weighed amounts of "purified," dry dithizone, must be determined. It is questionable whether dithizone has ever been obtained pure in the dry state.[4]

In an attempt to provide further evidence for a resolution of the disagreement on the formula of the lead–dithizone complex, Job's method of continuous variations,[6] which is quite different in principle from previous methods employed, was applied to the problem. The work of Tipton[7]

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(1) (a) Based upon a thesis submitted by J. O. Hibbits to the faculty of St. Louis University in partial fulfillment of the requirements for the Degree of Bachelor of Science. (b) To whom correspondence should be addressed.

(2) H. Fischer, *Z. angew. Chem.*, **42**, 1025 (1929).

(3) H. A. Liebhafsky and E. H. Winslow, THIS JOURNAL, **59**, 1966 (1937).

(4) P. A. Clifford, *J. Assoc. Offic. Agr. Chemists*, **26**, 26 (1943).

(5) H. Irving, E. I. Risdon and G. Andrew, *J. Chem. Soc.*, 537 (1949).

(6) P. Job, *Ann. Chem.*, **9**, 113 (1928).

(7) G. M. Tipton, S.J., Dissertation, St. Louis University, 1949 (to be published).

TABLE I

OPTICAL DENSITIES FOR VARYING COMPOSITIONS OF LEAD–DITHIZONE SOLUTIONS AT SEVERAL WAVE LENGTHS

x (mole fract. of dithizone)	Optical density Measured λ, mu → 500	510	520	530	540	Calculated[a] 500	510	520	530	540
0.2	0.120	0.126	0.123	0.102	0.089	0.031	0.022	0.021	0.027	0.034
.4	.229	.230	.229	.216	.174	.062	.043	.042	.054	.069
.6	.324	.344	.348	.324	.268	.094	.065	.063	.082	.103
.65	.372	.398	.406	.373	.312	.102	.070	.068	.089	.112
.675	.389	.406	.418	.380	.316	.106	.073	.071	.092	.116
.7	.367	.390	.396	.376	.312	.110	.075	.074	.095	.120
.8	.300	.316	.322	.309	.260	.125	.086	.085	.109	.138

[a] These values were calculated from the following molar extinction coefficients of dithizone: $\epsilon_{500} = 7800$, $\epsilon_{510} = 5400$, $\epsilon_{520} = 5300$, $\epsilon_{530} = 6800$, $\epsilon_{540} = 8600$.

and Sullivan[8] was used in the preparation of a pure dithizone solution of known concentration.

Theory

Theoretical considerations and derivations of equations involved in Job's method are presented in detail elsewhere.[9] A brief description is included here for the sake of defining necessary terms and symbols.

The formation of many complex ions may be represented by the reaction

$$A + nB \rightleftharpoons AB_n$$

in which A is a metal ion, and B is a molecule, such as ammonia, or an anion. If solutions of A and B, of the same molar concentrations, are mixed in varying proportions, and a suitable property of these solutions is measured, a curve may be constructed from which the number of molecules of B in the complex may be determined. The necessary curve is obtained by plotting Y, the difference between each value measured and the corresponding calculated value of the property had no interaction occurred, against the solution composition expressed in mole fraction of B. The value of n (the number of molecules of B in the complex) may be expressed as

$$n = x/(1 - x)$$

where x is the mole fraction of B at which Y is a maximum or a minimum. The property selected for this investigation was optical density.

Using the molar extinction coefficients ϵ_A, ϵ_B and ϵ_{AB_n}, it may be shown that when the concentration of AB_n in solution is a maximum, Y will be a maximum when $\epsilon_{AB_n} > (\epsilon_A + n\epsilon_B)$ or a minimum when $\epsilon_{AB_n} < (\epsilon_A + n\epsilon_B)$. For the conditions described by Vosburgh and Cooper in the special case where B is colorless, Y will be a maximum if $\epsilon_{AB_n} > \epsilon_A$, and a minimum if $\epsilon_{AB_n} < \epsilon_A$.

Experimental

Reagents.—A standard lead solution was prepared by dissolving a weighed amount of dried lead nitrate (Mallinckrodt A. R.) in conductance water (distilled water which had been redistilled from a basic permanganate solution), and diluting to a concentration of 2×10^{-5} M. The solution was made 10^{-3} M in nitric acid to prevent precipitation of basic lead salts.

A buffer solution[10] (pH 9.5) was prepared by dissolving ammonium nitrate (Mallinckrodt A.R.) in conductance water, and titrating to pH 9.5 with ammonium hydroxide (Mallinckrodt A.R.). The pH was measured with a glass electrode corrected for sodium error.

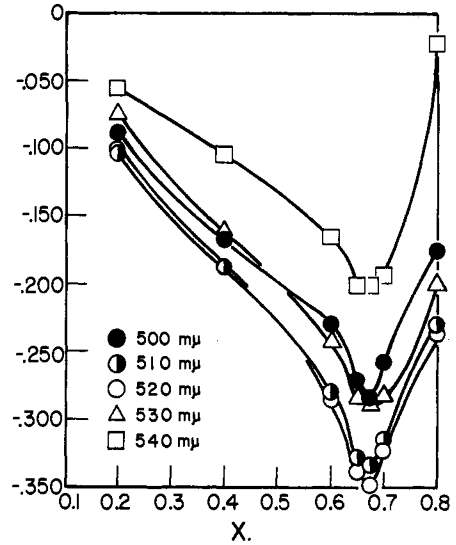

Fig. 1.—Optical density differences (Y) as a function of mole fraction of dithizone (X) from data in Table I.

Dithizone (Eastman Kodak Co.) was purified by shaking a carbon tetrachloride (Mallinckrodt A.R.) solution of the reagent with 1:100 ammonia, separating the layers, acidifying the aqueous layer with hydrochloric acid (Mallinckrodt A.R.) over a new carbon tetrachloride layer, and extracting the pure dithizone into the organic phase. It has been shown[7] that the ratio of optical densities at 620 and 450 mμ for a very pure dithizone solution should be equal to or greater than 1.65. Ratios obtained which are less than this value arise from oxidation products absorbing at 450 mμ. Experimental ratios for dithizone solutions prepared as described were 1.61 and 1.57, which are slightly less than the minimum 1.65 ratio, but the solutions stripped water-white, showing that the amount of oxidation product was negligible.[11] The optical densities of the solutions were measured at 620 mμ, and concentrations were calculated from the molar extinction coefficient,[12] $\epsilon_{620} = 34{,}600$. A 2×10^{-5} M solution was prepared by dilution; it was stored in a dark, refrigerated room to prevent decomposition.

Apparatus.—All glass equipment was cleaned with a sulfuric acid–nitric acid mixture, rinsed with distilled water, and steam-cleaned with conductance water.

Optical density measurements were made with a Cenco–Sheard spectrophotelometer, using 1-cm. cells, against a reference solution of carbon tetrachloride.

Procedure.—"Solutions," with total concentrations of lead and dithizone always equal to 1×10^{-5} M, were prepared from various amounts of standard lead and dithizone solu-

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[8] Sister M. L. Sullivan, Dissertation, St. Louis University, 1948.

[9] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[10] P. A. Clifford and H. J. Wichman, *J. Assoc. Offic. Agr. Chemists*, **19**, 130 (1936), have found 100% recovery of lead is obtained by extraction with excess dithizone at pH 9–11.

[11] F. J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 466.

[12] B. S. Cooper and Sr. M. L. Sullivan, *Anal. Chem.*, **23**, 613 (1951).

tions, buffer and carbon tetrachloride in the following manner: to x ml. of the lead solution were added $15 - x$ ml. of buffer, $15 - x$ ml. of dithizone solution and x ml. of carbon tetrachloride. The immiscible phases were shaken and the lead dithizonate extracted into the organic layer. Optical density measurements were made on the organic layer at 500, 510, 520, 530 and 540 mμ.

The total concentration of lead plus dithizone in the organic phase would be 2×10^{-5} M if lead is completely extracted and any excess dithizone remains in this phase. In the solutions where lead is in excess and is not completely extracted, the contribution of lead in carbon tetrachloride to the optical density, were it possible to exist in this manner, is assumed to be zero.

Results and Discussion

The optical densities measured, and those calculated from molar extinction coefficient data[8] on the basis of no interaction, are given in Table I.

Values of Y obtained from observed and calculated data in Table I are plotted in Fig. 1 against mole fraction of dithizone.

It was found that above 0.667 mole fraction of dithizone, where the reagent is in excess, some of the dithizone was extracted into the aqueous phase. However, measurements of this partitioning showed the necessary mole fraction corrections to be very small, and the position of the minimum in Fig. 1 is not affected.

Conclusions

From the formula $n = x/(1 - x)$, it can be seen that for the formula of the complex to be PbDz, the minimum, when Y is plotted against x, must occur at $x = 0.5$, and for the formula to be $PbDz_2$, the minimum must occur at $x = 0.667$. Since the curves at all five wave lengths have minima at 0.667, the formula $PbDz_2$ is confirmed.

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OAK RIDGE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY COLLEGE OF MEDICINE]

The Cupric and Ferric Citrate Complexes[1]

BY ROBERT C. WARNER AND IONE WEBER

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The complexes formed between cupric or ferric ions and citric acid have been investigated as a function of pH by spectrophotometric and titrimetric methods. In each case a chelate having a ratio of citrate to metal ion of 1:1 is formed in which four protons have been displaced from the citric acid. This is achieved at a pH of about 3 in the case of the iron and at 6 to 7 in the case of copper. At pH values below these, other 1:1 complexes are also present in which fewer than four protons have been displaced by the metal ion. Values of the equilibrium constants for the formation of all species contributing significantly to the equilibria have been obtained.

In an investigation[2] of the formation of metal–protein complexes between ferric or cupric ions and conalbumin, citrate was used as a competitor for the metal in studying the dissociation of the complexes. A knowledge of the nature of the metal–citrate complexes and of their formation constants was required for the interpretation of the protein work. In spite of numerous investigations of these compounds, satisfactory information of this kind was not available, particularly over the pH range of interest to us. We have therefore reinvestigated these systems employing both spectrophotometric and titrimetric methods.

Bobtelsky and Jordan[3] have concluded that citrate and cupric ions form complexes in a molar ratio of 1:1 and that a proton is displaced from the hydroxyl group of citric acid in the formation of the complex at pH 7. These conclusions are in agreement with our results. However, their data do not define the nature of the complexes as a function of pH nor do they permit the derivation of formation constants. Other investigators have not correctly assessed the displacement of protons by the cupric ion[4a] or have limited their study to acid solutions.[4b]

The complexes formed between citrate and ferric ion have not been clearly defined in the neutral pH range. The proposals of Bobtelsky and his coworkers[5,6] for the existence of complexes with various ratios of citrate to iron have been criticized by Lanford and Quinan[7] and do not appear to be well founded. The latter workers demonstrated a 1:1 ratio in strongly acid solution and formulated their results in terms of a complex resulting from the displacement of two protons by a ferric ion. While our results confirm the 1:1 complex as the predominant species, three protons were found to be displaced by the iron in acid solution. At a higher pH this is followed by the displacement of a fourth proton as in the case of the cupric complex.

Experimental

Reaction mixtures were prepared in a series of volumetric flasks from standard solutions of cupric nitrate or ferric nitrate and citric acid. Standard sodium hydroxide or nitric acid was added in varying quantity to cover the desired pH range. The ionic strength was calculated from a knowledge of the pH of each reaction mixture and the concentration of the various ionic species derived from preliminary experiments. It was then adjusted to 0.1 by the addition of sodium nitrate. This value was exceeded in some of the solutions in the iron series at the lowest and highest pH values. All experiments were run at a concentration of metal ion of 0.012 M for the copper series and 0.008 M for the iron series. These concentrations allowed

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[1] This work was carried out under contract with the Office of Naval Research.

[2] R. C. Warner and I. Weber, THIS JOURNAL, **75**, 5094 (1953).

[3] M. Bobtelsky and J. Jordan, *ibid.*, **67**, 1824 (1945).

[4] (a) L. Meites, *ibid.*, **72**, 180 (1950); (b) R. W. Parry and F. W. DuBois, *ibid.*, **74**, 3749 (1952).

[5] M. Bobtelsky and A. E. Simchen, *Compt. rend.*, **208**, 1646 (1939).

[6] M. Bobtelsky and J. Jordan, THIS JOURNAL, **69**, 2286 (1947).

[7] O. E. Lanford and J. R. Quinan, *ibid.*, **70**, 2900 (1948).